To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Thur 7/30/2015 6:04:17 PM
Subject: Re: dispersant

Hi Robyn,
Is there a time next week when we could chat about sharing dispersants? Thanks.
Mike

On Mon, Jul 20, 2015 at 9:21 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Hi Robyn,
> I just wanted to follow up on the possibility of sharing dispersants/shoreline cleaners...what you may have available to share and what we can share with you. Thanks.
> Mike
>
> On Fri, Jul 10, 2015 at 9:17 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:
>
>> Hi Robin,
>> We do have both. I suspect we have enough to share. I'll check and let you know early next week. One caveat...we'd have to the pull the material for you from a larger container. We didn't receive separate aliquots. Can that work?
>> Mike
>>
>> On Fri, Jul 10, 2015 at 9:00 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:
>>
>>> Hi Mike,
>>>
>>> I couldn't recall if you said your lab has finasol and corexit in stock for testing? If so, would you have any to share with us? We are running low and trying secure a liter or 2 of each.
>>>
>>> Thanks,
>>>
>>> Robyn
>>>
>>> <>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>
>>>
>>> Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

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Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief
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Biomolecular Research (CCEHBR)
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219 Fort Johnson Road
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e-mail: mike.fulton@noaa.gov http://www.chbr.noaa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Tue 4/14/2015 3:54:04 PM
Subject: dispersants

According to Elisha's spreadsheet, Advanced BioCatalytic Corp. is sending us a sample of Accell Clean.

Z. I. Chemicals has been contacted regarding ZI-400, but she hasn't received a response.

Sustainable Environmental Technology has also been contacted regarding Saf-Ron Gold.

That covers the 6 on the "magic" table.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

Cc: Holder, Edith[holder.edith@epa.gov]; Conmy, Robyn[Conmy.Robyn@epa.gov]
To: Bryan, Elisha[Bryan.Elisha@epa.gov]
From: zichemicals@mac.com
Sent: Fri 4/24/2015 12:46:05 AM
Subject: Re: ZI-400 sample inquiry

Dear Elisha,
Thanks for the clarification. Kindly note that I'm out of the country presently but your sample is ready to ship. Please ask your colleagues to communicate with me regarding this matter by email only if possible. I won't be back in LA 'til early June.

Best regards,

Barnaby Zelman
Z.I. Chemicals
----
email: zichemicals@mac.com
alt email: admin@zichemicals.com
Tel. 1.818.827.1301
Fax 1.818.479.8222
www.zichemicals.com

On Apr 23, 2015, at 9:48 AM, Bryan, Elisha <Bryan.Elisha@epa.gov> wrote:

Dear Barnaby,

Sorry about the delay. We would like to make the purchase. It is going through the proper channels and then the person in charge of purchasing will be in contact with you.

As for your question about the rule adoption, I have also forwarded it on through the proper channels to find out. I am still awaiting an answer or contact information.

Please let me know if you need anything else.

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.
On-Site Contractor to the U.S. EPA
ORD/NRMRL/LRPCD
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
Phone: 513-965-4805
Email: bryan.elisha@epa.gov

From: Barnaby Zelman <zichemicals@mac.com>
Sent: Wednesday, April 22, 2015 11:59 PM
To: Bryan, Elisha
Subject: Fwd: ZI-400 sample inquiry

Dear Elisha,

Awaiting your reply....

Thanks - Barnaby

Begin forwarded message:

From: Barnaby Zelman <zichemicals@mac.com>
Date: April 17, 2015 5:29:21 PM
To: "Bryan, Elisha" <Bryan.Elisha@epa.gov>
Cc: "inquiry@ZIChemicals.com" <inquiry@ZIChemicals.com>
Subject: Re: ZI-400 sample inquiry

Dear Elisha,

The cost, including UPS Ground service delivery of a 1 quart sample of our ZI-400 Oil Spill Dispersant made to order for the EPA would be $85. If this is acceptable please advise if you can issue payment via ACH, Wire transfer, or check (our last preference)?

May I ask one question...I could not find after cursory review of the link you provided where it mentions how long of a transition period would be allowed [after rule adoption] for manufacturers such as us to develop, test, submit, and list, the new products we will need to comply with the proposed revisions? For what it's worth, for us, we would like 2-3 years to be able to get any new products on the EPA listing before our existing product is removed. It's a matter of financial survival for small businesses such as ours and we do hope the EPA remains sensitive to this as well, given your own report indicated that 90% of current listed products are made by small businesses.

Thank you very much and awaiting your reply soonest.

Best regards,

Barnaby Zelman
Z.I. Chemicals
zichemicals@mac.com

On Apr 16, 2015, at 12:43 PM, "Bryan, Elisha" <Bryan.Elisha@epa.gov> wrote:

Good Afternoon,

The U.S. Environmental Protection Agency will be conducting a series of Dispersant Efficacy experiments using the newly proposed Baffled Flask Test for inclusion in the 40 CFR Appendix C to Part 300 Subpart J. I am a contractor with EPA's Office of Research and Development, National Risk Management Research Laboratory (NRMRL), Land Remediation and Pollution Control Division (LRPCD), working on this research.

As your product is listed on the U.S. EPA National Contingency Plan Product Schedule, we would like to include your product in our research and are interested in procuring a small quantity. I am contacting all manufacturers listed so that we can take into consideration the different characteristics of the dispersants.

This research will not change the current status of your product on the Product Schedule. More information on the proposed revisions and who to contact for comments can be found here: https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan#h-44.

Could you please send me a price quote for one liter / quart of *ZI-400*?

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

To: Musson, Steve[Musson.Steve@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Thur 5/14/2015 6:36:15 PM
Subject: RE: HASP Annual Review Due
2014-033 Oil Spill HASP_May2015.docx

Steve,

Enclosed is a revised HASP. During the last year we have received more oils, dispersants, and SWA. Those products have been added in tables by category at the end of the chemical list. There are no other changes.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Musson, Steve
Sent: Wednesday, May 13, 2015 10:09 AM
To: DelaCruz, Armah; Nadagouda, Mallikarjuna; Schaefer, Frank; Silvestri, Erin; Pressman, Jonathan; Wahman, David; Feldhake, David; quintero.maria@azdeq.gov; Shanks, Orin; Kelty, Catherine; Shoemaker, Jody; Varma, Rajender; Donohue, Maura; Pfaller, Stacy; Jewett, David; Hargrove, Kristie; Al-Abed, Souhail; Pinto, Patricio; Brooks, Michael; Wood, Lynn; Conmy, Robyn; Holder, Edith; Zaffiro, Alan; Batt, Angela; See, Mary Jean
Subject: HASP Annual Review Due

Everyone,

You are getting this email because your HASP is due for its annual review in May or June.

One of the staff listed below for each HASP, please take a moment to review the HASP and respond to this email by either:

1. State "The HASP is current and no changes need to be made"
2. State "The HASP is no longer necessary, please inactivate it"
3. Send the HASP back to me with any changes that need to be made to revise it.

Thanks,

Steve

Stephen Musson, PhD, CIH, CHMM

Safety, Health, and Environmental Management Program Manager

US EPA National Risk Management Research Laboratory

26 W. Martin Luther King Drive

Cincinnati OH 45268

513-569-7969

Division	HASP	Rev	Title	Date	Principal	Principal	Principal	Prepared	Branch	Expi

	#	#		Review Due	Investigator #1	Investigator #2	Investigator #3	Investigator		Date
MCE	20120 087	1	Cyanobacteria and their Cyanotoxins	6/16/2015	de la Cruz, Armah A.			de la Cruz, Armah A.	MiER	3/31/
WSW	20130 030	4	Sulfate and Phosphate Removal using novel synthesized media	6/17/2015	Mohan, Gayathri Ram	Nadagouda,Mallika		Mohan, Gayathri Ram	IO	3/31/
TCA	20132 033	2	Optimization of Bacillus anthracis Spore Recovery from Soil	6/18/2015	Schaefer, Erin	Shastri,		Feldhake, David	None Chosen	4/30/
WSW	20132 045	2	Chloraminated Drinking Water Distribution System Nitrification	5/15/2015	Pressman, Jonathan	Wahman,	David	Quinter, Kalya	TTEB	6/30/
WSW	20130 047	0	Genome Fragment Enrichment	6/30/2015	Shanks,	Orin		Kelty, Catherine	MCEB	6/30/
MCE	20130 062	0	Measuring Sucralose In Recreational Waters To Identify Human-Based Fecal Pollution: A Pilot Study	6/15/2015	Shoemaker,	Jody		Shoemaker, Jody	CERB	3/31/
STD	20140 003	0	Highly Selective Photosynthesis Processes over Visible-Light-Induced Micro- and Nano-structured Photocatalysts	5/29/2015	Baig, Nasir	Varma,	Rajender	Baig, Nasir	GPB	1/31/
MCE	20140 014	0	General Laboratory Practices Associated with Proteomic Research	5/30/2015	Donohue, Mauro	Pfaller,	Stacy	Donohue, Mauro	NERL	3/31/
GWER	20140 023	0	Laboratory 4	5/30/2015	Jewett,	David		Hargrove, Kristie	ARTSB	6/30/
LRPCD	20141 024	1	Metal Migration from Drinking Water Treatment Plant (DWTP) Sludges and Landfill Soils under Different Redox Conditions	6/4/2015	Abed,	Souhail		Pinto, Patricia	WMD	6/30/
GWER	20140 032	0	Predicting DNAPL Source Zone and Plume Response Using Site Measured Characteristics	6/30/2015	Brooks, Michael	Wood,	Lynn	Wood, Lynn	SRB	6/30/
LRPCD	20140 033	0	Oil Spill Research Including Work with Dispersants, Surface Washing Agents (SWAs), and Oil Degrading Microbes	6/30/2015	Lemmy,	Robyn		Holder, Elizabeth	ESMD	6/30/
SRMD	20140 039	0	Second Laboratory Demonstration for Microcystins in Drinking Water using Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry	6/30/2015	Adams,	William		Zaffiro, Alan	TSC	6/30/

EERD	2014-2016	0	Aquatic Studies Analytical Support using Solid Phase Extraction and Gas Chromatography/Mass Spectrometry	6/30/2015	Batt,Angela			See,Mary Jean	MIRD	6/30/

HASP #: 2014-033	Expiration Date: 06/30/2017

Health and Safety Plan

Title: Oil Spill Research Including Work with Dispersants, Surface Washing Agents (SWAs), and Oil Degrading Microbes
Principal Investigator(s): Robyn Conmy, Edith Holder
Office: ORD
Laboratory:
NRMRL Division:
LRPCD Branch:
ESMB
Building: AWBERC
Room/Lab #: 703, 701, 708, Constant Temperature Room 710
Start Date (Month / Year): May 2014
Estimated Research Completion Date (Month / Year): On Going*

Approvals

I have read and approve the attached Health and Safety Plan in conformance with the ORD Facility Chemical Hygiene Plan and Health & Safety Plan Policy. I certify that the workplace hazards, routinely and non-routinely encountered by employees, during the described activities, and for which Personal Protective Equipment has been provided, have been assessed for the determination of Personal Protective Equipment appropriateness, in compliance with 29 CFR 1910 Subpart I.

Name	Phone	Signature	Date
Edith Holder PREPARER	569-7178		
Dr. Robyn Conmy PRINCIPAL INVESTIGATOR	569-7090		
Dr. Joseph Schubauer-Berigan BRANCH CHIEF/DIVISION DIRECTOR	569-7734		
Dr. Steve Musson CHEMICAL HYGIENE OFFICER	569-7969		
Dr. Raghu Venkatapathy PTSI ON-SITE MANAGER	569-7077		

Though this research project has no definitive end date, the '**ORD NRMRL Procedure for the Development, Review and Approval of Project Specific Health and Safety Plans (HASPs)**'

Additional information on the completion of a Health & Safety Plan may be found at the SHEM website – Link available at: http://cincinnati.epa.gov/services/safety/

Project Description

Background:

Unintentional releases of oil into coastal waters may result in oil becoming stranded on shorelines. Oil that reaches the shoreline can have a severe effect on the local environment, including toxic exposures and smothering of biota in direct contact with the oil. Surface washing agents (SWAs) are chemical agents intended to enhance the removal of oil from shoreline surfaces, thereby minimizing detrimental effects to impacted biota. Dispersants are chemical agents intended to break up the oil by reducing the oil-water interfacial surface tension, which will eventually promote dispersion of oil droplets into the water column. It is necessary to evaluate the potential benefits as a remediation aide of these two classes of compounds as well as the long term ramifications to the environment of their use.

Indigenous bacteria have the capability of removing oil components by biodegradation. The capability of populations from different sources to biodegrade different oils as well as the interactions of microbial populations to the various dispersants and SWAs is a subject for current study.

Laboratory Activities

This laboratory has done previous studies looking at the effects of dispersants, SWA, bioremediation products, and microbes enriched from sediments and water. From an earlier QAAP 386-Q11-0, endorsed 7 June 2002: "The U.S. Environmental Protection Agency's (EPA) Oil Spill Research Program encompasses several major objectives: 1) to develop and/or conduct scientifically sound and defensible protocols for testing the effectiveness of commercial bioremediation products on crude and refined oil in various environments, 2) to develop and/or conduct chemical and microbiological methods for characterizing changes in the chemical and biological composition of oil-contaminated matrices, such as beach material, soil, or water; and 3) to conduct research defining the proper conditions needed to bring about oil spill cleanup in the field. Research to address these objectives was initiated under Quality Assurance Project Plan (QAPP)ID No. C-781-B. The work performed earlier used Alaskan oil and Alaskan cultures. The current research will include Gulf of Mexico oil and cultures, as well as other oils of interest such as Dilbit and freshwater cultures from the Enbridge spill in Kalamazoo, MI. If new spills occur, oil and sediments from the impacted site may come under investigation.

Analysis of oil in water will be measured by Fluorometry. Samples of oil that have been extracted into either methylene chloride or hexane will be measured using UV/Vis Spectrophotometry or GC/MS. The current work will use the methods listed in the following QAPPs and HASPS which can be found on the L drive under L:Public\NRMRL-PUB\Holder\OilSpill\HASP&QAPP:

\QAPP 490-Q5-0.doc Development of a Surface Washing Agent Testing Protocol endorsed October 2004 Amendment to QAPP 490-Q5-0 submitted November 2009, resubmitted to WAM July 2010 and to QA September 2010

\Natural Substrate SOP.doc The Natural Substrate Protocol for Determining Effectiveness of Surface Washing Agents

\SOP UV vis.doc Analysis of Oil Concentration in DCM by UV/VIS Spectrophotometry

\FDOM analysis.doc Standard Operating Protocol for Fluorescent Dissolved Organic Matter (FDOM)

In subdirectory QAPP 2013:
QAPP L-14866-QP-1-6 Development and Revision of Procedures for the Code of Federal Regulations (CFR) Appendix C to Part 300, Oil Spill Product Testing Protocols

Appendix A: Oil Dispersant Testing, Standard Operating Procedure for Determining Effectiveness of Oil

Dispersants Using the Baffled Flask Test, May 2013

Appendix B: Bioremediation Product Testing, Standard Operating Procedure for the Bioremediation Agent Effectiveness Test Protocol, May 2013

Appendix C: Oil Analysis SOPs, GC/MS procedures, May 2013
SOP 1: Glassware Cleaning Procedure for Oil Spill Projects
SOP 2: Preparation of Surrogate Recovery Standards
SOP 3: Preparation of Internal Standard Solution
SOP 4: Preparation of Working Standards, Check Standards, and Oil Standards for GC/MS Consistency.
SOP 5: GC/MS Method for the Analysis of Crude Oil Samples

A QAPP for specific research utilizing fluorescence spectrometry will be developed when this research is initiated.

A majority of the analytical methods are common to multiple projects and activities conducted within the oil spill program. The analytical work covered under this HASP include experiments with oil dispersants, surface washing agents (SWA), and oil degrading bacteria enriched from natural sources. Abiotic testing of the dispersants and SWA testing will utilize different oils and different products, varying parameters of application, temperature, weathering effects, and substrate. Biotic experiments will include biodegradation studies using a sacrificial shake flask experimental design.

The instruments that will be used for measuring oil components are a Shimadzu UV 1800 Spectrophotometer, Horiba Fluorolog3 Spectrofluorometer, WetLabs, Inc. ECO Submersible Fluorometer, and Agilent 6890 Gas Chromatograph with a 5973 Mass Spectrometer Detector. For all experiments, solvent (water, dichloromethane (DCM) or hexane) extracts of oil will be produced for analytical measurement.

Room 703 is the base lab for the various activities. The GC/MS will be located in room 708. CTR 710 will be used for 5oC work and 708 for work at 25oC. Storage of oil is in 703, storage of frozen samples is in 701, and storage of refrigerated samples is in 701 and CTR 710.

The full notice regarding dichloromethane (DCM) is given at the end of this document.

Physical Hazards Summary

(The physical hazards marked below(X) have been identified as present during the performance of the project. Job hazards for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.) The RSO shall be included in the list of reviewers/approval for all plans incorporating radioactive materials, radioactive devices, or radiation sources.

Physical Hazards		**Physical Hazards**	
Electrical Hazards		Noise	
Radioactive Materials		Temperature	x
Non-Ionizing Radiation		Illumination	
Ionizing Radiation		Compressed Gas	x
Heavy Lifting		Sharp Objects / Tools	
Vibration		Slips, Trips, Falls	
UV light/radiation			
Other (Specify) Rotating Equipment (Laboratory Shaker)			x

PPE Summary

(The PPE items marked below (X) are required to be utilized during performance of the project. PPE requirements for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.) Click here to review full PPE descriptions at OSHA's website

Face / Eye Protection	
Safety Glasses w/ Side Shields	x
Chemical Splash Goggles	x
Face Shield	x
Other (specify)	
Ear Protection	
Ear Plugs (Foam Inserts)	
Both Ear Plugs and Ear Muffs	
Ear Muffs	
Other (specify)	
Hand Protection	
Chemical – Nitrile disposable exam	x
Chemical - Latex disposable exam	
Chemical – Butyl disposable exam	
Chemical - Silver Shield®	x
Chemical – Ansel Barrier®	
Cotton	
Leather	
Cut Resistant (Kevlar ®)	
Other (specify) – thermal protective	x
Other (specify) – Polypropylene Gloves (see FDOM SOP)	x
Protective Clothing	
Lab Coat	x
Lab Apron	
Jumpsuit	
Shoe covers	
Oversleeves	
Other (specify)	

Equipment Requirements

The safety equipment/engineering controls marked below(X) are required to be utilized during performance of the project. Requirements for specific steps are described in the Job Hazard Analysis Table at the end of the HASP.

Chemical Fume Hood	x
Biological Safety Cabinet	
Walk-in / Bulking Hood	
Radiological Fume Hood	
Balance Enclosure	
Clear Air Bench (laminar flow hood)	
Spot Ventilation Unit (Snorkel)	
Local Exhaust Ventilation	
Canopy Hood	
Liquid Scintillation Counter	
Refrigerator / Freezer	x
Deep Freezer	x

Other (specify) – spectrophotometer / shaker / GC/MS/ drying oven and muffle furnace	x

Chemicals to be Used

Federal law under SARA, Title III, (also known as the Emergency Planning and Community Right to Know Act) requires that Material Safety Data Sheets (MSDS) be readily available for every chemical in the facility. EPA utilizes an online service to assist in meeting this requirement: http://epa.chemwatch.us User Name:epa; Password: cfr1910CW. If the MSDS is not available through Chemwatch, a hardcopy of the manufacturer supplied MSDS must accompany the HASP.

Item #	Chemical Name	CAS#	Project Use	Disposal Method for Unused Chemicals	MSDS Availability:
			Ex. Reagent, Standard, or Specific task #	S = Sink T = Trash W = Chemical Waste Program	**C**:Chemwatch **H**:Hardcopy
1	Dichloromethane	75-09-2	Solvent	W	C
2	Hexane	110-54-3	Solvent	W	C
3	Petroleum Crude Oil	8002-05-9	Reagent	W	H
4	Aquaclean	34590-94-8	Surface Washing	W	H
5	EC9580A COREXIT 9580	64742-47-8	Surface Washing	W	H
6	PetroClean		Surface Washing	W	H
7	Petrotech 25		Surface Washing	W	H
8	Biosolve		Surface Washing	W	H
9	Superall #38		Surface Washing	W	H
10	Corexit 9500		Dispersant	W	H
11	Biodispers		Dispersant	W	H
12	Dispersit SPC1000		Dispersant	W	H
13	Finasol OSR52		Dispersant	W	H
14	JD-2000		Dispersant	W	H
15	NEOS AB3000		Dispersant	W	H
16	Sodium Sulfate	7757-82-6	Reagent	W	C
17	Sea Salts (Sigma) (or Instant Ocean)	Mixture	Media	S or T	C
18	Bushnell-Haas Broth		Media	S or T	N/A
19	Sodium Chloride	7647-14-5	Media	S	C
20	Potassium Chloride	7447-40-7	Media	S	C
21	Potassium Bromide	7758-02-3	Media	W	C
22	Sodium Borate	1303-96-4	Media	S	C
23	Magnesium Chloride	7791-18-6	Media	S or T	C
24	Calcium Chloride	10043-52-4	Media	S or T	C
25	Strontium Chloride	10476-85-4	Media	W	C
26	Sodium Bicarbonate	7757-82-6	Media	S or T	C
27	Potassium Nitrate	7757-79-1	Media	W	C
28	Iron Chloride	10025-77-1	Media	W	C
29	Sodium Tripolyphosphate	7722-88-5	Media	W	C
30	Sodium Hydroxide	1310-73-2	reagent	Neutralize 6 < pH < 9	C
31	Hydrochloric Acid	7647-01-0	Reagent, acid washing, fluorometry	Neutralize 6 < pH < 9	C

32	Acenaphthene	00083-32-9	standard	W	C
33	Acenaphthylene	00208-96-8	standard	W	C
34	Benzo(a)anthracene	00056-55-3	standard	W	C
35	Biphenyl	00092-52-4	standard	W	C
36	2,6-Dimethylnaphthalene	00581-42-0	standard	W	C
37	3,6-Dimethylphenanthrene	01576-67-6	standard	W	C
38	1-Methylnaphthalene	00090-12-0	standard	W	C
39	2-Methylphenanthrene	02531-84-2	standard	W	C
40	2,3,5-Trimethylnaphthalene	02245-38-7	standard	W	C
41	Decane	00124-18-5	standard	W	C
42	Undecane	01120-21-4	standard	W	C
43	Dodecane	00112-40-3	standard	W	C
44	Tridecane	00629-50-5	standard	W	C
45	Tetradecane	00629-59-4	standard	W	C
46	Pentadecane	00629-62-9	standard	W	C
47	Hexadecane	00544-76-3	standard	W	C
48	Heptadecane	00629-78-7	standard	W	C
49	Octadecane	00593-45-3	standard	W	C
50	Nonadecane	00629-92-5	standard	W	C
51	Eicosane	00112-95-8	standard	W	C
52	Heneicosane	00629-94-7	standard	W	C
53	Docosane	00629-97-0	standard	W	C
54	Tricosane	00638-67-5	standard	W	C
55	Tetracosane	00646-31-1	standard	W	C
56	Pentacosane	00629-99-2	standard	W	C
57	Hexacosane	00630-01-3	standard	W	C
58	n-Heptacosane	00593-49-7	standard	W	C
59	Octacosane	00630-02-4	standard	W	C
60	n-Nonacosane	00630-03-5	standard	W	C
61	n-Triacontane	00638-68-6	standard	W	C
62	n-Hentriacontane	00630-04-6	standard	W	C
63	n-Dotriacontane	00544-85-4	standard	W	C
64	n-Tritriacontane	00630-05-7	standard	W	C
65	n-Tetratriacontane	14167-59-0	standard	W	C
66	n-Pentatriacontane	00630-07-9	standard	W	C
67	Naphthalene	00091-20-3	standard	W	C
68	Fluorene	00086-73-7	standard	W	C
69	Dibenzothiophene	00132-65-0	standard	W	C
70	Phenanthrene	00085-01-8	standard	W	C
71	Fluoranthene	00206-44-0	standard	W	C
72	Pyrene	00129-00-0	standard	W	C
73	Chrysene	00218-01-9	standard	W	C
74	Benzo(b)fluoranthene	00205-99-2	standard	W	C
75	Benzo(k)fluoranthene	00207-08-9	standard	W	C
76	Benzo(e)pyrene	00192-97-2	standard	W	C
77	Benzo(a)pyrene	00050-32-8	standard	W	C
78	Perylene	00198-55-0	standard	W	C
79	Indeno(1,2,3-cd)pyrene	00193-39-5	standard	W	C
80	Dibenzo(a,h)anthracene	00053-70-3	standard	W	C

81	Benzo(g,h,i)perylene	00191-24-2	standard	W	C
82	Pristane	01921-70-6	standard	W	C
83	Phytane	00638-36-8	standard	W	C
84	Anthracene	00120-12-7	standard	W	C
85	Benzo[*b*]naphtho[2,1[*d*]thiophene	239-35-0	standard	W	C
86	5b-Cholestane	481-20-9	standard	W	C
87	5a-Androstane	438-22-2	standard	W	C
88	Hopane	1176-44-9	standard	W	C
89	D22 n-Decane	16416-29-8	standard	W	C
90	D34 n-Hexadecane	15716-08-2	standard	W	C
91	D42 n-Eicosane	62369-67-9	standard	W	C
92	D62 n-Triacontane	93952-07-9	standard	W	C
93	D8-Naphthalene	1146-65-2	standard	W	C
94	D10-Anthracene	1719-06-8	standard	W	C
95	D12-Chrysene	1719-03-5	standard	W	C
96	D12-Perylene	1520-96-3	standard	W	C
97	D36-Heptadecane	39756-35-9	standard	W	C
98	D50-Tetracosane	16416-32-3	standard	W	C
99	D66-Dotriacontane	62369-68-0	standard	W	C
100	D10-1-methylnaphthalene	1517-22-2	standard	W	C
101	D10-Phenanthrene	1517-22-2	standard	W	C
102	D10-Pyrene	1718-52-1	standard	W	C
103	Ph buffers 4, 7, and 10	Varies	Calibration	S	C
104	Nitric Acid	7697-37-2	pH adjustment/ sand washing	Neutralize 6 < pH < 9	C
105	Methanol	67-56-1	fluorometry	W	C
106	Rhodamine B	81-88-9	fluorometry	W	C
107	Ethylene Glycol	107-21-1	fluorometry	W	C
108	Quinine Sulfate Dihydrate	6119-70-6	fluorometry	W	C
109	Sulfuric Acid	7664-93-9	Fluorometry, pH adjustment	Neutralize 6 < pH < 9	C
110	Dimethyldichlorosilane (5%) in Toluene		Silanizing glassware	W	C
111	Sodium Azide		Microbial Growth Inhibitor	W	C
112	Magnesium Sulfate		Media	S or T	C
113	Manganese Sulfate		Media	S or T	C
114	Boric Acid		Media	S or T	C
115	Zinc Sulfate		Media	S or T	C
116	Ammonium Molybdate		Media	S or T	C
117	Potassium Hydrogen Phosphate		Media	S or T	C
118	Potssium dihydrogen Phosphate		Media	S or T	C

Current Inventory of Crude Oils Line Item # 3 (May 2015)		
Anadarko	Endicott	Prudhoe Bay
ANS	Endicott (18% evaporated)	PXP 01
ANS 521	Esgravos	PXP 02
Arabian Light	FO2	Rock
BHP Billiton	Fuel 6	South Louisiana

Bonnie Light	Harmony	Sweet Synthetic
Bunker C	IFO 120	Terra Nova
Dilbit, Cold Lake	IFO 380	Venoco E-10
Dilbit, WCS	North Star	Venoco E-19
Doba	PER 038	
Elly	PER 040	

Current Inventory of Oil Spill Dispersants Line Items # 10-15 (May 2015)		
Accell Clean DWD	Finasol OSR52	Saf-Ron Gold
Corexit 9500	JD-2000	SX-100
Dispersit SPC1000	Nokomis 3-AA	ZI-400
FFT Solution	Nokomis 3-F4	

Current Inventory of Oil Spill Surface Washing Agents Line Items # 4-9 (May 2015)		
ADP7	F500	Petroluxus
Aquaclean	Gold Crew SW	Petrotech 25
BG-Clean 401	Green Beast	Premier 99
Biosolve	Jep Marine Clean	Procleans PCR 107
CleanGreen Planet Wash	Marine Green Clean	Sandklene 9500
Corexit 9580	Marine Green Clean Plus	SC-1000
Cytosol	Naturama G3 A-5	Simple Green
Dynamic Green	Nokomis 5W	Spillclean
Enviroclean	Nontox SWA	Superall #38
EPA Oil Field Solution™	Petro-Clean	

Biological Research

Does the project in any way involve manipulation of recombinant DNA?	No
If yes, are all proposed activities specifically exempted from the NIH Guidelines for Research Involving Recombinant DNA Molecules?	
Does the project in any way involve human subjects or biological materials obtained from human subjects?	No
If yes, is the project exempt from the Health and Human Services Policy for Protection of Human Subjects?	
Does the project involve animals requiring Institutional Animal Care & Use Committee (IACUC) approval? (includes vertebrate & invertebrates animals)	No

Biological Agents

(The Biosafety Level (BSL) and Animal Biosafety Level (ABSL) refer to specific combinations of work practices, safety equipment, and facility design elements utilized to minimize exposure of workers and the environment to infectious agents. Principal Investigators must perform an agent risk assessment to determine the BSL.)

Item #	Biological Agent (list all that apply)	BSL #	Source of Biological Agent	Vaccination Required?
1	Oil degrading bacteria isolated from environmental samples	1	Water or sediments	no

Waste Management

DCM, hexane, methanol, and crude oil wastes (dissolved in DCM) from analytical samples collected via separatory

funnel, standards, and glassware rinsate should be disposed of through the SHEM hazardous wastes program due to solvent, oil and PAH contents. After washing gravel and sand with DCM, the DCM is drained into the waste container and the substrate is placed in the fume hood to allow the remaining DCM to evaporate off, before disposing of the cleaned substrate in the garbage.

Spent silanizing solution should be disposed throught the SHEM hazardous waste program.

Original chemical reagents will be disposed as indicated in the chemical use table.

Any remaining fresh or seawater will be disposed of down the sink drain because no known hazardous wastes are involved.

Aqueous waste remaining after removal of DCM using a separatory funnel may be sink disposed. Any remaining DCM is placed in a hazardous waste container before dumping remaining water to sink.

Acid solution from sand/gravel cleaning will be collected and neutralized using sodium hydroxide to a pH between 5 and 9 and then disposed of down the sink.

Will Hazardous Waste Be Generated? yes Will the Treatability Exemption be Utilized? no

Sample Management

All samples will be labeled with sample descriptors including date, analyst, and constituents (solutes and solvents). They will be stored in the refrigerators in 701 or CTR710. They will be kept until data is approved and then disposed of using the Chemical Waste Program. Any enriched bacterial consortia will be frozen and kept in the -80 freezer in 701. They may be maintained indefinitely.

Hexane containing samples are flammable and should only be stored in refrigerators or freezers designed and labeled as approved for flammable material storage.

Spill Response

General spills are handled in accordance with the Chemical Hygiene Plan found at http://intranet.epa.gov/nerlintr/shem/lab_safety/docs/ChemHygiene.pdf

Small spills shall be wiped up by project personnel wearing proper PPE and the absorbent material bagged, labeled as to its hazardous constituents, then submitted to the SHEM Waste Program for proper disposal. In the event of a large solvent spill, SHEM will be contacted via x7997 or by way of security per the Chemical Hygiene Plan.

The spill of any bacterial consortia that have been enriched from environmental samples will be doused with either a 10% chlorine solution or 70% ethanol solution, allowed to sit for ~ 10 minutes and then wiped up. The wipes used will be placed in a biohazard bag for autoclaving.

The chemical spill kit is located: 701, 703, 708 - on the left side of the lab near the door. 710 – May use a spill kit from the other laboratories

Authorized Personnel

Training and medical monitoring requirements will vary depending on the complexity and materials used in the process. Therefore, only personnel appropriately trained and monitored will be permitted to work under this plan. To be "authorized", employees must have completed the training and screenings selected below.

Mandatory for all researchers

Initial Laboratory Safety	**X**
Current Chemical Hygiene Plan Laboratory Safety Refresher	**X**
Hazardous Waste Management (RCRA)	**X**
Medical Surveillance	**X**
Project/Task Dependent	
Respiratory Protection	
Biosafety / Blood borne Pathogens	
Initial Field Safety and/or 8 hour field safety refresher training in the last 12 months	
40 - hour HAZWOPER and/or 8 hour HAZWOPER refresher in the last 12 months	
Hearing Protection	
First Aid / CPR / AED	
DOT Hazardous Materials Awareness/Shipment	
Radiation Safety	
Other (specify) review attached methylene chloride awareness	**X**
Forklift Operator	
Climbing/Scaffolding	

References:

Laboratory Staff Concurrence

I have read, understood and will comply with all the requirements of the attached Health and Safety Plan, MSDS's, and the rules contained in the U. S. EPA- Facilities Chemical Hygiene Plan. I have also had the opportunity to ask any questions, and had my questions satisfactorily answered prior to my beginning work under this plan.

Date	Name (Print)	Government Employee	Other (Specify)	Signature

General Activities
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Room / Area	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Preparation of artificial seawater and freshwaters	703	Little chemical hazard as it consists of salts. Irritants	Prepare chemical solutions in a CFH where possible	Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes
Use of freezer	701	Thermal burns from the ultra low freezer	Use caution when handling items from the freezer	Thermal protective gloves Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes
Use of autoclave	380	See chemical hygiene plan for Autoclave Hazard Analysis	See chemical hygiene plan for Autoclave Hazard Analysis	See chemical hygiene plan for Autoclave Hazard Analysis
Use of centrifuge		See chemical hygiene plan for Centrifuge Hazard Analysis	See chemical hygiene plan for Centrifuge Hazard Analysis	See chemical hygiene plan for Centrifuge Hazard Analysis
Preparation of dilute acid from concentrated acid for performing pH adjustments	703	Splash – chemical burns to exposed skin	Prepare solution in a chemical fume hood	Face shield – Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes
Use of drying oven and muffle furnace	703	Burns	Caution with hot glassware. Let muffle furnace completely cool down before removing glassware.	Thermal protective gloves
CTR 710		Limited ventilation – build up of chemical vapors, inhalation of DCM and other toxic and carcinogenic chemical vapors	No open chemical container work should be performed in CTR 710. All containers should remain closed. Samples should be moved to a room with a CFH if necessary to open.	Lab coat, safety glasses with side shields, nitrile gloves, closed-toe shoes

HASP #: 2014-033 Expiration Date: 06/30/2017

Job Hazard Analysis
SOP 1 Glassware Washing

Glassware Washing *** includes supplies, utensils and containers in contact with soil, extraction fluid, and/or leachate**		
Sequence of Basic Job Steps	**Potential Hazards**	**Recommended Action or Procedure**
Rinse loose debris from the surface	- Cross contamination from glassware to personnel – potential exposure - Splash or spray from rinsing – potential exposure - Potential breakage of glassware from cracks or defects – cuts / lacerations / contamination	- Inspect glassware before cleaning for cracks or other damage – discard in broken glass container if damage is noticed or suspected - ensure proper PPE is worn for material handling (minimum of protective eyewear, laboratory coat, and appropriate gloves) - use low pressure water to avoid splash and/or aerosolization of the contaminants - if any glassware is broken during cleaning – only remote means should be used to pick up any broken glass
Wash with brush, soap, and water. Triple rinse with water. Soak in soap bath.	- Cross contamination from glassware to personnel – potential exposure - Splash or spray from rinsing – potential exposure - Potential breakage of glassware from cracks or defects – cuts / lacerations / contamination	- Inspect glassware before cleaning for cracks or other damage – discard in broken glass container if damage is noticed or suspected - ensure proper PPE is worn for material handling (minimum of protective eyewear, laboratory coat, and appropriate gloves) - use low pressure water to avoid splash and/or aerosolization of the contaminants - if any glassware is broken during cleaning – only remote means should be used to pick up any broken glass
Drying object using drying racks	- potential for dropping the glassware, tools, etc. – breakage, spillage, contact with other surfaces - slip / trip / fall hazards from water spillage or splashing from the rinsing process	- ensure that the drying racks are placed appropriately to reduce any ergonomic hazard from stretching, or repetitive motion - follow the established emergency procedures for injuries or spills including immediate notification of your supervisor or 911 for life threatening cases (also x7777, direct contact to security)

SOP 2 -Preparation of a Surrogate Recovery Standard
Job Hazard Analysis, Controls, and PPE
SOP 3 - Preparation of Internal Standard Solution
Job Hazard Analysis, Controls, and PPE
SOP 4 - Preparation of Working Standards, Check Standards, and Oil Standards for GC/MS
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Weigh reagents **Dissolve reagents / wash beakers using methylene chloride** **Transfer the solution**	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and take care to not cross contaminate. DCM – attempt to not 'pour' DCM as the ST is low and tends to spread. Use the sash on a CFH for splash protection where possible. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Pipetting	see chemical hygiene plan for pipetting recommendations	See chemical hygiene plan for pipetting recommendations	Double nitrile gloves and / or silvershield gloves (where dexterity is not an issue). Lab coat, safety glasses with side shields, and closed-toe shoes.

SOP 5 - GC/MS Method for the Analysis of Crude Oil
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Compressed Gas Usage (Helium)	See Chemical Hygiene Plan – JHA for Compressed Gas Cylinders	See Chemical Hygiene Plan – JHA for Compressed Gas Cylinders	See Chemical Hygiene Plan – JHA for Compressed Gas Cylinders
Solvent / standard / stock preparation	See JHA for SOP 2, 3, and 4)	See JHA for SOP 2, 3, and 4)	See JHA for SOP 2, 3, and 4)
GC Operation	Compressed Gases GC venting of toxic analytes	Ensure GC exhaust is routed to laboratory ventilation.	Lab coat, safety glasses, protective gloves

SOPs

Analysis of Oil Concentration in DCM by UV/Vis Spectrophotometry and Spectrofluorometry

Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Add DCM to crude oil **Syringe use** **Extraction with DCM (shaking and venting)** **Dispense / transfer solutions**	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and take care to not cross contaminate. DCM – attempt to not 'pour' DCM as the ST is low and tends to spread. Use the sash on a CFH for splash protection where possible. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Pipetting	See chemical hygiene plan for pipetting recommendations	See chemical hygiene plan for pipetting recommendations	Double nitrile gloves and / or silvershield gloves (where dexterity is not an issue). Lab coat, safety glasses with side shields, and closed-toe shoes.
Operation of Spectrophotometer and Fluorometer	UV light exposure	Ensure all appropriate equipment guards are present and operable.	Nitrile gloves Lab coat, safety glasses with side shields, and closed-toe shoes.

SOP

The Baffled Flask Test for Determining Effectiveness of Dispersants

Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Add DCM to crude oil and seawater **Syringe use** **Extraction with DCM (shaking and venting)** **Dispense / transfer solutions**	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and take care to not cross contaminate. DCM – attempt to not 'pour' DCM as the ST is low and tends to spread. Use the sash on a CFH for splash protection where possible. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Pipetting	See chemical hygiene plan for pipetting recommendations	See chemical hygiene plan for pipetting recommendations	Double nitrile gloves and / or silvershield gloves (where dexterity is not an issue). Lab coat, safety glasses with side shields, and closed-toe shoes.
Extraction with DCM including shaking and venting	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for	Perform extraction in a chemical fume hood only. Handle reagents in the smallest quantities possible and take care to not cross contaminate. Use the sash	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side

	illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	on a CFH for splash protection where possible. This should **ONLY** be done in a CFH.	shields, and closed-toe shoes.
Operation of Spectrophotometer or Spectrofluorometer	UV light exposure	Ensure all appropriate equipment guards are present and operable.	Nitrile gloves Lab coat, safety glasses with side shields, and closed-toe shoes.
Use of the shaker	Spills, mechanical issues with equipment	Ensure all appropriate equipment guards are present and operable. Ensure a periodic inspection of equipment.	Nitrile gloves Lab coat, safety glasses with side shields, and closed-toe shoes.

SOP - Natural Substrate Protocol
Job Hazard Analysis, Controls, and PPE

Job Step/Operation	Potential Hazards/Risks	Recommended Action/Procedure	PPE Required
Acid wash of the substrate	burns from acid contact from spills, splashes or careless use of bath	Conduct in chemical fume hood	Double nitrile gloves - Wear normal length nitrile gloves inside of elbow length nitrile gloves; Wear a face shield / chemical splash goggles.
Addition of crude oil	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn) – see chemical hygiene plan for pipetting recommendations	Prepare the reagents / standards in a chemical fume hood only. Handle reagents in the smallest quantities possible and take care to not cross contaminate. Use the sash on a CFH for splash protection where possible. – see chemical hygiene plan for pipetting recommendations. Review OSHA Regulated Substance Awareness for DCM.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
Use of the shaker	skin chemical contact from splash or spill - eye chemical contact inhalation of chemicals contact injury with moving/rotating machinery	Work in a chemical fume hood when handling reagents with respiratory warnings Work in a chemical fume hood Ensure area is clear before starting shaker. Secure loose fitting clothing to prevent snagging by shaker.	wear a laboratory coat, and nitrile gloves; wear chemical splash goggles
DCM extraction	Reagents listed contain materials that are listed as carcinogens or potential for causing cancer, irritants, and are photosensitizers. Potential for illness upon inhalation and / or skin contact (chemical dermatitis, increase probability for sunburn)	Perform extraction in a chemical fume hood only. Handle reagents in the smallest quantities possible and take care to not cross contaminate. Use the sash on a CFH for splash protection where possible. This should **ONLY** be done in a CFH.	Double gloves - Wear normal length nitrile gloves over silvershield gloves to maintain dexterity; Lab coat, safety glasses with side shields, and closed-toe shoes.
UV spectrophotometry	eye chemical contact inhalation of chemicals skin chemical contact from splash or spill	Work in a chemical fume hood when handling reagents with respiratory warnings Handle quartz cuvet carefully	wear a laboratory coat, and nitrile gloves; wear chemical splash goggles

Methylene chloride
DCM

CAS No: 75-09-2
RTECS No: PA8050000
UN No: 1593
EC No: 602-004-00-3

CH_2Cl_2
Molecular mass: 84.9

TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Combustible under specific conditions. Gives off irritating or toxic fumes (or gases) in a fire.		In case of fire in the surroundings: use appropriate extinguishing media.
EXPLOSION	Risk of fire and explosion (see Chemical Dangers).	Prevent build-up of electrostatic charges (e.g., by grounding).	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		**PREVENT GENERATION OF MISTS! STRICT HYGIENE!**	
Inhalation	Dizziness. Drowsiness. Headache. Nausea. Weakness. Unconsciousness. Death.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Artificial respiration may be needed. Refer for medical attention.
Skin	Dry skin. Redness. Burning sensation.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse and then wash skin with water and soap.
Eyes	Redness. Pain. Severe deep burns.	Safety goggles, face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
Ingestion	Abdominal pain. (Further see Inhalation).	Do not eat, drink, or smoke during work. Wash hands before eating.	Rinse mouth. Do NOT induce vomiting. Give plenty of water to drink. Rest.

SPILLAGE DISPOSAL	PACKAGING & LABELLING	
Personal protection: filter respirator for organic gases and vapours. Do NOT let this chemical enter the environment. Ventilation. Collect leaking and spilled liquid in sealable containers as far as possible. Absorb remaining liquid in sand or inert absorbent and remove to safe place.	Xn Symbol R: 40 S: (2-)23-24/25-36/37 UN Hazard Class: 6.1 UN Pack Group: III	Do not transport with food and feedstuffs.

EMERGENCY RESPONSE	SAFE STORAGE
Transport Emergency Card: TEC (R)-61S1593 NFPA Code: H2; F1; R0	Separated from metals (see Chemical Dangers), food and feedstuffs. Cool. Ventilation along the floor.

IMPORTANT DATA

Physical State; Appearance
COLOURLESS LIQUID, WITH CHARACTERISTIC ODOUR.

Physical dangers
The vapour is heavier than air. As a result of flow, agitation, etc., electrostatic charges can be generated.

Chemical dangers
On contact with hot surfaces or flames this substance decomposes forming toxic and corrosive fumes. Reacts violently with metals such as aluminium powder and magnesium powder, strong bases and strong oxidants causing fire and explosion hazard. Attacks some forms of plastic rubber and coatings.

Occupational exposure limits
TLV: 50 ppm as TWA; A3 (confirmed animal carcinogen with unknown relevance to humans); BEI issued; (ACGIH 2004).

MAK: Carcinogen category: 3A; (DFG 2004).

Routes of exposure
The substance can be absorbed into the body by inhalation and by ingestion.

Inhalation risk
A harmful contamination of the air can be reached very quickly on evaporation of this substance at 20°C.

Effects of short-term exposure
The substance is irritating to the eyes, the skin and the respiratory tract. Exposure could cause lowering of consciousness. Exposure could cause the formation of methaemoglobin.

Effects of long-term or repeated exposure
Repeated or prolonged contact with skin may cause dermatitis. The substance may have effects on the central nervous system and liver. This substance is possibly carcinogenic to humans.

PHYSICAL PROPERTIES

Boiling point: 40°C
Melting point: -95.1°C
Relative density (water = 1): 1.3
Solubility in water, g/100 ml at 20°C: 1.3
Vapour pressure, kPa at 20°C: 47.4
Relative vapour density (air = 1): 2.9
Relative density of the vapour/air-mixture at 20°C (air = 1): 1.9
Auto-ignition temperature: 556°C
Explosive limits, vol% in air: 12-25

Octanol/water partition coefficient as log Pow: 1.25

ENVIRONMENTAL DATA

This substance may be hazardous in the environment; special attention should be given to ground water contamination.

NOTES

Addition of small amounts of a flammable substance or an increase in the oxygen content of the air strongly enhances combustibility.
Depending on the degree of exposure, periodic medical examination is suggested.
The odour warning when the exposure limit value is exceeded is insufficient.
Do NOT use in the vicinity of a fire or a hot surface, or during welding.
R30 is a trade name.

Card has been partly updated in April 2005. See section Occupational Exposure Limits.

To: BOL-Deshpande, Ruta (deshpars)[deshpars@mail.uc.edu]
Cc: BOL-Zhang, Yu (zhang4y5)[zhang4y5@mail.uc.edu]; Holder, Edith[holder.edith@epa.gov]; BOL-Zhuang, Mobing (zhuangmg)[zhuangmg@mail.uc.edu]; Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Campo-Moreno, Pablo (campomp)
Sent: Mon 6/8/2015 7:10:37 PM
Subject: Re: Result of Finasol Experiment

Ruta,

Could you please send over your data along with your SARA chromatograms?
Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
Fax: (513)-556-4162
campomp@ucmail.uc.edu

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.
The adventures for Sherlock Holmes

On Jun 8, 2015, at 3:07 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Thank you for sending and for the update!

Pablo, can you send to Edie and I the figures from the dilbit and ANS degradation results? We didn't walk away with our hard copies. Also, Ruta's SARA plots would be helpful too.

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

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727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Zhang, Yu (zhang4y5) [mailto:zhang4y5@mail.uc.edu]
Sent: Monday, June 08, 2015 1:34 PM
To: Conmy, Robyn; Holder, Edith
Cc: Campo-Moreno, Pablo (campomp); Zhuang, Mobing (zhuangmg)
Subject: Result of Finasol Experiment

Hi! Robyn and Edith.

Please find the Finasol result in the attachment. Let me know if there is any problem with it. Thanks!

Regards,

Yu

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Campo-Moreno, Pablo (campomp)
Sent: Thur 7/30/2015 2:43:49 PM
Subject: Re: CHEM36329 Editor decision - revise

Robyn,

Finally good news about the JD-2000 paper. Chemosphere has accept it with a minor revision: we need to add a conclusion at the end of the paper (see below)
Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
Fax: (513)-556-4162
campomp@ucmail.uc.edu

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.
The adventures for Sherlock Holmes

On Jul 30, 2015, at 5:51 AM, Suidan, Makram (suidanmt) <SUIDANMT@UCMAIL.UC.EDU> wrote:

On 7/30/15, 12:36 PM, "Chemosphere" <chem-eo@elsevier.com> wrote:

Dear Dr. Suidan,

I can now inform you that the reviewers and editor have evaluated the manuscript "Effect of Dispersants on the Biodegradation of South Louisiana Crude Oil at 5 and 25 °C" (Dr. Makram T Suidan). I am pleased to say that it has been favourably received and publication with minor revision is recommended (see below and on http://ees.elsevier.com/chem/).

I look forward with interest to receipt of the modified version. You

should explain how and where each point of the reviewers' comments has been incorporated. For this, use submission item "Revision Notes" when uploading your revision. Also, indicate the changes in marked changes version of the revised manuscript (submission item "Revision, changes marked"). Should you disagree with any part of the reviews, please explain why.

To facilitate further review, lines in this manuscript should be consecutively numbered.

Please strictly follow the formatting requirements as presented in the Guide for Authors.

As it is in the interest of authors to have a short turnaround time, we kindly ask you to submit the revised manuscript as soon as possible but within 21 DAYS. If the revised manuscript is not submitted before the deadline, the manuscript will be considered withdrawn.

To submit a revision, go to http://ees.elsevier.com/chem/ and log in as an author. You will find your submission record under Submission(s) Needing Revision.

For guidelines on how to submit your revised manuscript please go the following address:
http://help.elsevier.com/app/answers/detail/p/7923/a_id/91

When submitting your revised manuscript, please ensure that you upload the source files (e.g. Word). Uploading a PDF file at this stage will create delays should your manuscript be finally accepted for publication. If your revised submission does not include the source files, we will contact you to request them.

When resubmitting, please present any figures, tables etc. as separate files. See the Artwork Guidelines on the home page right menu for further file naming conventions, referencing and format issues.

I hope that you will find the comments to be of use to you and am looking forward with interest to receiving your revision.

NOTE: Upon submitting your revised manuscript, please upload the source files for your article. For additional details regarding acceptable file formats, please refer to the Guide for Authors at:
http://www.elsevier.com/journals/chemosphere/0045-6535/guide-for-authors

When submitting your revised paper, we ask that you include the following items:

Response to Reviewers (mandatory)

This should be a separate file labeled "Response to Reviewers" that carefully addresses, point-by-point, the issues raised in the comments appended below. You should also include a suitable rebuttal to any specific request for change that you have not made. Mention the page, paragraph, and line number of any revisions that are made.

Manuscript and Figure Source Files (mandatory)

We cannot accommodate PDF manuscript files for production purposes. We also ask that when submitting your revision you follow the journal formatting guidelines. Figures and tables may be embedded within the source file for the submission as long as they are of sufficient resolution for Production. For any figure that cannot be embedded within the source file (such as *.PSD Photoshop files), the original figure needs to be uploaded separately. Refer to the Guide for Authors for additional information.
http://www.elsevier.com/journals/chemosphere/0045-6535/guide-for-authors

Highlights (mandatory)

Highlights consist of a short collection of bullet points that convey the core findings of the article and should be submitted in a separate file in the online submission system. Please use 'Highlights' in the file name and include 3 to 5 bullet points (maximum 85 characters, including spaces, per bullet point). See the following website for more information
http://www.elsevier.com/highlights

Graphical Abstract (optional)

Graphical Abstracts should summarize the contents of the article in a concise, pictorial form designed to capture the attention of a wide readership online. Refer to the following website for more information:
http://www.elsevier.com/graphicalabstracts

Please note that this journal offers a new, free service called AudioSlides: brief, webcast-style presentations that are shown next to published articles on ScienceDirect (see also http://www.elsevier.com/audioslides). If your paper is accepted for publication, you will automatically receive an invitation to create an AudioSlides presentation.

Please note that we allow 60 days for the first author revision and 45 days for any additional author revisions that are required.

Chemosphere features the Interactive Plot Viewer, see: http://www.elsevier.com/interactiveplots. Interactive Plots provide easy access to the data behind plots. To include one with your article, please prepare a .csv file with your plot data and test it online at http://authortools.elsevier.com/interactiveplots/verification before submission as supplementary material.

Thank you for submitting your work to this journal.

Kind regards,
Prof. Yu Liu
Editor
Chemosphere

.....
Important note: If a reviewer has provided a review or other materials as attachments, those items will not be in included in this letter. Please ensure therefore that you log on to the journal site and check if any attachments have been provided.

COMMENTS FROM EDITORS AND REVIEWERS

Reviewer #1: In this research paper, authors have reported quantitative biodegradability of a primary component in the oil spill dispersant JD-2000, in the presence and absence of crude oil.
The findings are unique and significant enough for publication. The manuscript is well prepared.
However, it would be good to provide a conclusion at the end of the paper which is somehow missing from the manuscript.

.....
Author's Checklist

Please follow this checklist to avoid another round of review. The best way is to refer to Chemosphere website for author's guidelines.

MS Number
Add Chemosphere code number in all your correspondence.

Abstract/Text
The page limitation has to be followed. Unless specified differently by the editor the number of tables plus figures should not exceed seven.

Text
Follow the format with respect to unit, section headings, line numbers, etc.
Delete all well known equations (e.g., 1st-order reaction, isotherms, etc.).

Units
Use SI units; follow the correct format (e.g., mg kg-1).
Use M for mol/L; d for days, h for hours, min for minutes, etc.
Be consistent! Use uppercase L for l (litre).

Syntax
Please always leave a space between number and SI unit (e.g. 4.6 mm, 21 °C, 24 h etc.),
however no space before the "%", "/" and ":" signs. Moreover, provide an adequate space in
between words.
Use periods for decimal points.
Don't use italics to highlight text or reference literature. Italics should be used for
Latin/Greek expressions only.

Acronyms
Define acronyms when they first appear; thereafter directly use them.
Again: be consistent!
Do not create new acronyms.
Don't use improper names for chemicals, e.g., "dioxins" for PCDD
No need to define if they are no longer used.
No need to define simple chemical formulas.

Math
Slash equations in Text/Tables [e.g., (a)/c), but stack numerators over denominators e.g.,
a
--- in equations.
C
Use numerical numbers 1, 2, etc, for equations.

Citation
Use author-date format. For one author, use author's name; for 2 authors, spell out the

names of both authors; for 3 or more than 3 authors, use et al. All cited references must be listed.
Follow the chronological order.

References
Use abbreviated journals (see the ISI list under (http://library.caltech.edu/reference/abbreviations/, which is freely accessible).
Delete all issue numbers for consistency.
Capitalize the 1st letter of each word for books/reports/thesis; use lowercase letters for paper titles.

Tables/Figures
Follow the format; numbered sequentially.
Give a list of the figure captions on a separate page.

Significant figures
Consider the reproducibility of your results (errors in sampling, extraction and
measurements) when presenting data.

****
For further assistance, please visit our customer support site at http://help.elsevier.com/app/answers/list/p/7923. Here you can search for solutions on a range of topics, find answers to frequently asked questions and learn more about EES via interactive tutorials. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Ryan, Scott A[Scott.Ryan@dfo-mpo.gc.ca]; King, Thomas L[Tom.King@dfo-mpo.gc.ca]
From: Robinson, Brian
Sent: Fri 9/11/2015 8:44:19 PM
Subject: Updated Fluorometry Plots and Downstream LISST Data
LISST Contour Plots Summary (LISST#2).docx
LISST DSD Plots Summary (LISST#2).docx
Stacked Fluorometry Plots Summary (updated).docx

Hi Robyn,

Scott was able to pull off a miracle and get all of the data reprocessed! I can still see the smoke rising out of his computer…

Attached please find an updated file with the stacked fluorometry plots. As requested, all of the plots now have the same format – even if there was no data collected from a particular instrument. The plots also start at 1 min.

The second and third files contain the data from the downstream LISST (contour plots and PSD plots). Scott's script generated some summary plots that I think can be used to compare the upstream and downstream instruments…I'll tackle that on Monday. On Monday I should also have the methods document ready to send…Tom is reviewing it this weekend. Another 10+ pages for the report, without pictures.

This weekend I'm tackling the VOC data…I think it is all starting to come together!

Brian

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: McClellan, Kim
Sent: Wed 9/23/2015 6:50:42 PM
Subject: Updates on Peer-Reviewed Journal Articles in STICS

Hi Robyn,

At your convenience, can you update (has the article been published, not published, being revised and resubmitted to the same journal or resubmitted to a different journal) me on these peer-reviewed journal articles, so that I can update your record in STICS.

Complete Citation and Review	Robyn Conmy	Devi Sundaravadivelu	ORD-011145	Evaluation of Surface Characteristics of Oil Spill Solidifiers	Peer Reviewed	5/15/2015 4:48 PM	
Complete Citation and Review	Robyn Conmy	Lin Zhao	ORD-009856	Evaluation of Turbulence Structures in Laboratory Baffled Flasks Under Different Mixing Energy: Implications for Dispersant Effectiveness Testing	Peer Reviewed	5/15/2015 4:36 PM	
Complete Citation and Review	Robyn Conmy	Devi Sundaravadivelu	ORD-011143	Parametric Study to Determine the Effect of Temperature on Oil Solidifier Performance and the Development of a New Empirical Correlation for Predicting Effectiveness	Peer Reviewed	5/15/2015 4:36 PM	
Complete Citation and Review	Robyn Conmy	Mobing Zhuang	ORD-011135	Biodegradability of Different Initial Concentrations of Alaska North Slope Crude Oil Dispersed with Corexit C9500	Peer Reviewed	5/15/2015 4:34 PM	
Level 2 Approval	Robyn Conmy	Robyn Conmy	ORD-004300	Performance of Submersible Optical Sensors Exposed to Chemically-Dispersed Crude Oil: Wave Tank Simulations for Improved Oil Spill Monitoring	Peer Reviewed	5/5/2015 3:00 PM	Albert Venosa
Complete Citation and Review	Kim McClellan	Devi Sundaravadivelu	ORD-[illegible]	Effect of Operational Variables on the Performance of Oil Solidifiers under a Newly	Peer Reviewed	3/31/2014 2:20 PM	

			Developed Testing Protocol using a Light, Medium and Heavy Oil	
Complete Citation and Review	Robyn Conmy	Mobina Zhuang	A Comparative Study on the Biodegradability of Crude Oil Dispersed With JD-2000 at 5 and 25 degrees C	Peer Reviewed 9/19/2014 8:54 PM [redacted]
Complete Citation and Review	Kim Mcclellan	Shuyun Wu	Anaerobic Biodegradation of Soybean Biodiesel and Diesel Blends under Methanogenic Conditions	Peer Reviewed 2/12/2015 8:35 PM
Complete Citation and Review	Robyn Conmy	Shuyun Wu	Anaerobic biodegradation pattern of flaxseed biodiesel and diesel blends	Peer Reviewed 2/20/2015 11:59 AM

Thanks,

Kim

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: SantoDomingo, Jorge
Sent: Tue 7/28/2015 5:12:27 PM
Subject: Re: oil funds for genomics work

Got it. I just heard that the guy that was going to give me a quote is on vacation. I will send him an email to see if he can help me with the numbers. I think that we can accommodate some of the samples with Finasol but I need to double check. I sent a PR for consumables, so I'll follow up on this as well.

Talk to you soon. jorge

From: Conmy, Robyn
Sent: Tuesday, July 28, 2015 7:03 AM
To: SantoDomingo, Jorge
Subject: oil funds for genomics work

Hi Jorge,

We budgeted for $80K of expiring funds (FY14) and tentatively I have $40K of FY15 budgeted for work during FY16. Haven't gotten a recent burn rate from Pegasus or Michael Moeykens, but that $80K was still intact as of last month. Consumables would be added to this amount, not a portion of this, but we would need to confirm with Raghu on how much is available. We are underspent on the work assignment, so ordering more supplies should not be an issue.

Please let me know what is needed so I can coordinate with Raghu.

Thanks,

Robyn

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Robyn N. Conmy, Ph.D.

Research Ecologist

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513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Colon, Betzy
Sent: Tue 4/14/2015 1:12:49 PM
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

The shorter version should work, but it wouldn't hurt to have your full CV in case we need more info. If you could send both, that would be great!

Thanks again,

Betzy

From: Conmy, Robyn [mailto:Conmy.Robyn@epa.gov]
Sent: Tuesday, April 14, 2015 9:09 AM
To: Colon, Betzy
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Do you want the full cv or the 2 page version that gets submitted with LOIs and proposals to BSEE?

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Research Ecologist

USEPA/NRMRL/LRPCD

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727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Colon, Betzy [mailto:BColon@versar.com]
Sent: Tuesday, April 14, 2015 9:07 AM
To: Conmy, Robyn
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Robyn,

Would it be possible for you to send me an electronic copy of your CV today? It can be a draft version if that helps. I'm getting ready to send BSEE our initial list of reviewers, but also need to include a brief summary of their background/qualifications.

Thanks so much,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

From: Colon, Betzy
Sent: Thursday, April 9, 2015 12:00 PM
To: 'Conmy, Robyn'
Cc: Schubauer-Berigan, Joseph; Gilliland, Alice
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Robyn,

I am glad to hear that you are interested and available to participate as a reviewer. I will send you some additional information in a separate email.

Alice, thank you again for forwarding my email along.

Best regards,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

From: Conmy, Robyn [mailto:Conmy.Robyn@epa.gov]
Sent: Thursday, April 9, 2015 9:54 AM
To: Colon, Betzy
Cc: Schubauer-Berigan, Joseph; Gilliland, Alice
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hello Ms. Colon,

I am happy to serve as a reviewer for the BSEE report.

Cheers,

Robyn

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Robyn N. Conmy, Ph.D.

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conmy.robyn@epa.gov

From: Gilliland, Alice
Sent: Thursday, April 09, 2015 8:17 AM
To: Conmy, Robyn
Cc: Schubauer-Berigan, Joseph
Subject: FW: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Robyn,

Can you please reach out to Betzy Colon next week (after you return) if you have time to be a peer reviewer on this?

Thanks,

Alice

From: Colon, Betzy [mailto:BColon@versar.com]

Sent: Wednesday, April 08, 2015 3:32 PM
To: Gilliland, Alice
Subject: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Alice,

I tried leaving a message on your phone but not sure if I was successful. I may have hung up before the message was saved. The reason I contacted you is because we are conducting a peer review for the Bureau of Safety and Environmental Enforcement (BSEE) on dispersants and wanted to see if someone from your team might be interested in participating as a reviewer. I know Dr. Venosa used to conduct research in this area but not sure if someone from EPA has taken over this research after he retired.

I provided specific information below on the peer review. Feel free to forward to anyone on your team who may be able to participate in this peer review.

Thank you,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Email: bcolon@versar.com

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>>

My name is Betzy Colon and I work for an environmental consulting firm that is supporting the Department of the Interior (DOI) Bureau of Safety and Environmental Enforcement (BSEE) in conducting an external peer review of the draft document titled "Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment." The peer review will be a letter peer review with no teleconference or in-person meeting required. I am writing to see if you would be interested in participating in the peer review scheduled to begin in early May.

BACKGROUND:

BSEE has requested an external peer review of the draft report entitled "Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment," which was prepared by BSEE. Part of BSEE's research is committed to ensuring that functional, safe, and environmentally responsible oil spill response methods are identified and used under appropriate conditions. Understanding oil spill response technologies for use in the Arctic is crucial for the U.S. government and industry to develop robust spill response plans. In February of 2014, BSEE conducted independent dispersant effectiveness testing to compare available formulations. Several products were tested under mesoscale simulated arctic conditions at the Ohmsett facility. The study was conducted in order to better understand and compare the effectiveness of various dispersants under simulated Arctic test conditions. Four dispersants were selected from the EPA's NCP Product Schedule and tested on an Alaskan crude oil: Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, and ZI 400.

The objective of this letter-style peer review is for BSEE to receive written comments from individual experts on the scientific merit of the report, appropriateness of the methods used, quality of the data, and the overall strengths and limitations of the study.

LENGTH OF PAPERS:

-

The draft document to be reviewed contains approximately 25 pages of main text, including tables and figures, and 55 pages of references and appendices.

-

DUTIES OF REVIEWER:

-

Your primary function as a peer reviewer would be to evaluate and provide written comments on the document and answer seven charge questions.

We are identifying approximately six to seven scientific experts from which five will be selected to serve as peer reviewers. The reviewers will be senior scientists with expertise/experience in oil spill response in Arctic waters and a demonstrated understanding of the methods utilized to understand the efficacy/effectiveness of chemical dispersant use.

TIMELINE:

We are expecting to select reviewers within the next few weeks in preparation to begin the review in early May. Reviewers will have approximately six weeks to complete their reviews and prepare written comments, following receipt of the materials and charge questions.

-

COMPENSATION:

An honorarium is being provided for the peer review and will be discussed if you are interested

and available to participate in the review.

-

NEXT STEPS:

If you are interested in participating, please provide the following information:

1. An electronic copy of your CV.

2. Complete contact information (address, phone number, email).

3. Whether you will be entering this agreement as a consultant or a subcontractor through your company (subcontract - only applicable for those people that work for companies).

Once I've received the information requested above, I will send you our conflict of interest questions for you to answer and return via e-mail, along with forms requiring your signature. Before participating, you will need to confirm that there are no conflict of interest issues, either real or perceived.

We are hoping to make selections within the next few weeks and, as a result, would appreciate a prompt response from you.

Thanks, and I look forward to hearing from you.

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

To: Barnaby Zelman[zichemicals@mac.com]
Cc: Holder, Edith[holder.edith@epa.gov]; Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Bryan, Elisha
Sent: Thur 4/23/2015 4:48:41 PM
Subject: Re: ZI-400 sample inquiry

Dear Barnaby,

Sorry about the delay. We would like to make the purchase. It is going through the proper channels and then the person in charge of purchasing will be in contact with you.

As for your question about the rule adoption, I have also forwarded it on through the proper channels to find out. I am still awaiting an answer or contact information.

Please let me know if you need anything else.

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Barnaby Zelman <zichemicals@mac.com>
Sent: Wednesday, April 22, 2015 11:59 PM
To: Bryan, Elisha
Subject: Fwd: ZI-400 sample inquiry

Dear Elisha,

Awaiting your reply....

Thanks - Barnaby

Begin forwarded message:

From: Barnaby Zelman <zichemicals@mac.com>
Date: April 17, 2015 5:29:21 PM
To: "Bryan, Elisha" <Bryan.Elisha@epa.gov>
Cc: "inquiry@ZIChemicals.com" <inquiry@ZIChemicals.com>
Subject: Re: ZI-400 sample inquiry

Dear Elisha,

The cost, including UPS Ground service delivery of a 1 quart sample of our ZI-400 Oil Spill Dispersant made to order for the EPA would be $85. If this is acceptable please advise if you can issue payment via ACH, Wire transfer, or check (our last preference)?

May I ask one question...I could not find after cursory review of the link you provided where it mentions how long of a transition period would be allowed [after rule adoption] for manufacturers such as us to develop, test, submit, and list, the new products we will need to comply with the proposed revisions? For what it's worth, for us, we would like 2-3 years to be able to get any new products on the EPA listing before our existing product is removed. It's a matter of financial survival for small businesses such as ours and we do hope the EPA remains sensitive to this as well, given your own report indicated that 90% of current listed products are made by small businesses.

Thank you very much and awaiting your reply soonest.

Best regards,

Barnaby Zelman
Z.I. Chemicals
zichemicals@mac.com

On Apr 16, 2015, at 12:43 PM, "Bryan, Elisha" <Bryan.Elisha@epa.gov> wrote:

Good Afternoon,

The U.S. Environmental Protection Agency will be conducting a series of Dispersant Efficacy experiments using the newly proposed Baffled Flask Test for inclusion in the 40 CFR Appendix C to Part 300 Subpart J. I am a contractor with EPA's Office of Research and Development, National Risk Management Research Laboratory

(NRMRL), Land Remediation and Pollution Control Division (LRPCD), working on this research.

As your product is listed on the U.S. EPA National Contingency Plan Product Schedule, we would like to include your product in our research and are interested in procuring a small quantity. I am contacting all manufacturers listed so that we can take into consideration the different characteristics of the dispersants.

This research will not change the current status of your product on the Product Schedule. More information on the proposed revisions and who to contact for comments can be found here: https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan#h-44.

Could you please send me a price quote for one liter / quart of *ZI-400*?

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Wed 9/2/2015 12:42:13 PM
Subject: Re: dispersant

Will do. Thanks!

On Tue, Sep 1, 2015 at 3:16 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Let's say 9:30 ET. Since you will have a group, just call my office number.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

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Research Ecologist

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conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Tuesday, September 01, 2015 3:10 PM

To: Conmy, Robyn
Subject: Re: dispersant

By the way, if possible I'd like to have a couple other folks sit in.

Mike

On Tue, Sep 1, 2015 at 3:00 PM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Thanks Robyn. Sometime Thursday morning would work.
>
> Mike
>
> On Tue, Sep 1, 2015 at 12:10 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:
>
> > Hi Mike,
> >
> > Never a pest! I am tied up with meetings today and tomorrow. Would Thursday work for you?
> >
> > <>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>
> >
> > Robyn N. Conmy, Ph.D.
> >
> > Research Ecologist
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> >
> > 513-431-1970 (EPA mobile)
> >
> > 727-692-5333 (Personal mobile)
> >
> > conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Tuesday, September 01, 2015 10:34 AM
To: Conmy, Robyn
Subject: Re: dispersant

Hi Robyn,

Sorry to be a pest, but it would be great if we could arrange to chat about dispersants, cleaners and bioremediation agents. Thanks.

Mike

On Wed, Aug 19, 2015 at 9:28 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Hi Robyn,
>
> I hope you're well. Would you have some time in the next week or so to discuss our joint interest in dispersants, shoreline cleaners,and bioremediation agents? Thanks.
>
> Mike

> On Thu, Jul 30, 2015 at 2:04 PM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:
>
> > Hi Robyn,
> >
> > Is there a time next week when we could chat about sharing dispersants? Thanks.
> >
> > Mike

> > On Mon, Jul 20, 2015 at 9:21 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:
> >
> > > Hi Robyn,

I just wanted to follow up on the possibility of sharing dispersants/shoreline cleaners...what you may have available to share and what we can share with you. Thanks.

Mike

On Fri, Jul 10, 2015 at 9:17 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

Hi Robin,

We do have both. I suspect we have enough to share. I'll check and let you know early next week. One caveat...we'd have to the pull the material for you from a larger container. We didn't receive separate aliquots. Can that work?

Mike

On Fri, Jul 10, 2015 at 9:00 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Mike,

I couldn't recall if you said your lab has finasol and corexit in stock for testing? If so, would you have any to share with us? We are running low and trying secure a liter or 2 of each.

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

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conmy.robyn@epa.gov

--

Dr. Michael H. Fulton-Estuaries and Land Use Branch Chief

Center for Coastal Environmental Health and

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To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Colon, Betzy
Sent: Tue 4/14/2015 1:07:28 PM
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Robyn,

Would it be possible for you to send me an electronic copy of your CV today? It can be a draft version if that helps. I'm getting ready to send BSEE our initial list of reviewers, but also need to include a brief summary of their background/qualifications.

Thanks so much,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Fax: (703) 642-6809

Email: bcolon@versar.com

Visit us at: www.versar.com

From: Colon, Betzy
Sent: Thursday, April 9, 2015 12:00 PM
To: 'Conmy, Robyn'
Cc: Schubauer-Berigan, Joseph; Gilliland, Alice
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Robyn,

I am glad to hear that you are interested and available to participate as a reviewer. I will send you some additional information in a separate email.

Alice, thank you again for forwarding my email along.

Best regards,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Fax: (703) 642-6809

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From: Conmy, Robyn [mailto:Conmy.Robyn@epa.gov]
Sent: Thursday, April 9, 2015 9:54 AM
To: Colon, Betzy
Cc: Schubauer-Berigan, Joseph; Gilliland, Alice
Subject: RE: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hello Ms. Colon,

I am happy to serve as a reviewer for the BSEE report.

Cheers,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

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727-692-5333 (mobile)

conmy.robyn@epa.gov

From: Gilliland, Alice
Sent: Thursday, April 09, 2015 8:17 AM
To: Conmy, Robyn
Cc: Schubauer-Berigan, Joseph
Subject: FW: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Robyn,

Can you please reach out to Betzy Colon next week (after you return) if you have time to be a peer reviewer on this?

Thanks,

Alice

From: Colon, Betzy [mailto:BColon@versar.com]
Sent: Wednesday, April 08, 2015 3:32 PM
To: Gilliland, Alice
Subject: BSEE Peer Review on the Testing of Four Dispersants in Simulated Arctic Conditions

Hi Alice,

I tried leaving a message on your phone but not sure if I was successful. I may have hung up before the message was saved. The reason I contacted you is because we are conducting a peer review for the Bureau of Safety and Environmental Enforcement (BSEE) on dispersants and wanted to see if someone from your team might be interested in participating as a reviewer. I know Dr. Venosa used to conduct research in this area but not sure if someone from EPA has taken over this research after he retired.

I provided specific information below on the peer review. Feel free to forward to anyone on your team who may be able to participate in this peer review.

Thank you,

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Mobile: (352) 514-5471

Fax: (703) 642-6809

Email: bcolon@versar.com

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>>>

My name is Betzy Colon and I work for an environmental consulting firm that is supporting the Department of the Interior (DOI) Bureau of Safety and Environmental Enforcement (BSEE) in conducting an external peer review of the draft document titled "Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment." The peer review will be a letter peer review with no teleconference or in-person meeting required. I am writing to see if you would be interested in participating in the peer review scheduled to begin in early May.

BACKGROUND:

BSEE has requested an external peer review of the draft report entitled "Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment," which was prepared by BSEE. Part of BSEE's research is committed to ensuring that functional, safe, and environmentally responsible oil spill response methods are identified and used under appropriate conditions. Understanding oil spill response technologies for use in the Arctic is crucial for the U.S. government and industry to develop robust spill response plans. In February of 2014, BSEE conducted independent dispersant effectiveness testing to compare available formulations. Several products were tested under mesoscale simulated arctic conditions at the Ohmsett facility. The study was conducted in order to better understand and compare the effectiveness of various dispersants under simulated Arctic test conditions. Four dispersants were selected from the EPA's NCP Product Schedule and tested on an Alaskan crude oil: Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, and ZI 400.

The objective of this letter-style peer review is for BSEE to receive written comments from individual experts on the scientific merit of the report, appropriateness of the methods used, quality of the data, and the overall strengths and limitations of the study.

LENGTH OF PAPERS:

-

The draft document to be reviewed contains approximately 25 pages of main text, including tables and figures, and 55 pages of references and appendices.

-

DUTIES OF REVIEWER:

-

Your primary function as a peer reviewer would be to evaluate and provide written comments on the document and answer seven charge questions.

We are identifying approximately six to seven scientific experts from which five will be selected to serve as peer reviewers. The reviewers will be senior scientists with expertise/experience in oil spill response in Arctic waters and a demonstrated understanding of the methods utilized to understand the efficacy/effectiveness of chemical dispersant use.

TIMELINE:

We are expecting to select reviewers within the next few weeks in preparation to begin the review in early May. Reviewers will have approximately six weeks to complete their reviews and prepare written comments, following receipt of the materials and charge questions.

-

COMPENSATION:

An honorarium is being provided for the peer review and will be discussed if you are interested and available to participate in the review.

-

NEXT STEPS:

If you are interested in participating, please provide the following information:

1. An electronic copy of your CV.

2. Complete contact information (address, phone number, email).

3. Whether you will be entering this agreement as a consultant or a subcontractor through your company (subcontract - only applicable for those people that work for companies).

Once I've received the information requested above, I will send you our conflict of interest questions for you to answer and return via e-mail, along with forms requiring your signature. Before participating, you will need to confirm that there are no conflict of interest issues, either real or perceived.

We are hoping to make selections within the next few weeks and, as a result, would appreciate a prompt response from you.

Thanks, and I look forward to hearing from you.

Betzy

Bethzaida Colon

Environmental Scientist

Environmental Services Group

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Fax: (703) 642-6809

Email: bcolon@versar.com

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To: Dyson, Brian[Dyson.Brian@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]; McClellan, Kim[Mcclellan.Kim@epa.gov]; Holder, Edith[holder.edith@epa.gov]; raghuraman.venkatapathy@ptsied.com[raghuraman.venkatapathy@ptsied.com]
From: Venkatapathy, Raghuraman
Sent: Fri 9/11/2015 5:46:03 PM
Subject: FW: 2016 GOMRI abstracts
Solidifier_Abstract 2016 GOMRI.DOCX
Dilbit-Abstract_2016 GOMRI.DOCX
FINASOL_Abstract_2016 GOMRI.DOCX
IFO120_Abstract_2016 GOMRI.DOCX

Hi Brian,

Thanks for agreeing to enter the attached abstracts into STICS on Robyn's behalf. Dick Brenner and Steve Wright can probably be listed as the two reviewers (if requested).

Thanks for your help!

raghu

Raghuraman Venkatapathy
On-Site Technical Manager
Pegasus Technical Services, Inc.
On-Site Contractor to U.S. EPA
NRMRL-STD/LRPCD, MS: 443
26 W. Martin Luther King Jr. Drive
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Phone: (513) 569 7077 (O)/(513) 549 7880 (GV)
Fax: (513) 569 7677.
e-mail: venkatapathy.raghuraman@epa.gov

raghuraman.venkatapathy@ptsied.com

From: Conmy, Robyn
Sent: Friday, September 11, 2015 12:11
To: Venkatapathy, Raghuraman
Cc: Holder, Edith; raghuraman.venkatapathy@ptsied.com; McClellan, Kim
Subject: RE: 2016 GOMRI abstracts

Hi Raghu,

Edie and I have cleared our abstracts through STICS already. These will also need clearance. Given the short time frame, they should get entered into STICS today. I am off site, can you or Edie reach out to Kim McClellan (POC for STICS for our division) to see if she can enter this for Pegasus? I have cc'd her.

Cheers,

Robyn

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Robyn N. Conmy, Ph.D.

Research Ecologist

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Cincinnati, Ohio 45268

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727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Venkatapathy, Raghuraman
Sent: Friday, September 11, 2015 11:19 AM
To: Conmy, Robyn
Cc: Holder, Edith; raghuraman.venkatapathy@ptsied.com
Subject: FW: 2016 GOMRI abstracts

Hi Robyn,

The abstracts prepared by UC are attached.

Thanks,

raghu

Raghuraman Venkatapathy
On-Site Technical Manager
Pegasus Technical Services, Inc.
On-Site Contractor to U.S. EPA
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Fax: (513) 569 7677.
e-mail: venkatapathy.raghuraman@epa.gov

raghuraman.venkatapathy@ptsied.com

From: Campo-Moreno, Pablo (campomp) [mailto:campomp@UCMAIL.UC.EDU]
Sent: Thursday, September 10, 2015 17:35
To: Raghu Venkatapathy
Subject: 2016 GOMRI abstracts

Raghu,

Attached please find the abstracts for GOMRI.

Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor

University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
Fax: (513)-556-4162
campomp@ucmail.uc.edu

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.
The adventures for Sherlock Holmes

2016 Gulf of Mexico Oil Spill and Ecosystem Science Conference

Biodegradability Of Diluted Bitumen Oil By Kalamazoo River Cultures In Freshwater

Ruta Suresh Deshpande[1], Pablo Campo-Moreno[1], Robyn N. Conmy[2]

1. Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, 2901 Woodside Drive, Cincinnati, OH 45221, USA

2. U.S. Environmental Protection Agency, National Risk Management Risk Laboratory, 26 W. MLK Drive Cincinnati, OH, 45268, USA

Petroleum products derived from the Canadian oil sands are in limelight due to the proposal of the Keystone pipeline expansion to the Gulf of Mexico and major spills (Kalamazoo, 2010 and Mayflower, 2013). Oil sands are unconventional petroleum deposits made of sand, clay, water and highly viscous bitumen. To make this bitumen transportable, it has to be either upgraded (synthetic crude) or diluted with diluents like naphtha, natural gas condensate, lower hydrocarbons (dilbit) or synthetic crude (synbit). Limited literature is available on the fate of dilbit when it is released to the environment thus, a study was conducted to check the biodegradability of dilbit using two types of dilbit, the Western Canadian Select and the Cold Lake at 5 °C and 25 °C. Tests were run for 60 days at 25 °C and for 72 days at 5 °C using cultures isolated from the Kalamazoo River sediments which were enriched on dilbit at 5 °C (cyro) and 25 °C (meso). The resultant samples for both the oils showed similar trends of biodegradation for alkanes and aromatics on analysis by GC-MS. Alkanes were absolutely degraded at both the temperatures. Nearly complete aromatics removal was observed at 25 °C, while more than 50 % removal was achieved at 5 °C. Also, a reduction in the hopane concentration was observed at 25 °C whereas at 5 °C the hopane concentration remained constant. Results of this study will contribute to understand and model the behavior of dilbit when it is exposed to the environment.

Keywords: oil sands, diluted bitumen, biodegradation

Biodegradation of Finasol OSR 52 and Dispersed Alaska North Slope Crude Oil at 5 °C and 25 °C

Yu Zhang[1], Pablo Campo[1],
Ruta Suresh Deshpande[1], Mobing Zhuang[1], and Robyn N. Conmy[2]

1. Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, 2901 Woodside Drive, Cincinnati, OH 45221, USA

2. U.S. Environmental Protection Agency, National Risk Management Risk Laboratory, 26 W. MLK Drive Cincinnati, OH, 45268, USA

Abstract

A study was conducted with Finasol OSR 52 dispersant and Alaska North Slope (ANS) crude oil in sterile GP2 artificial seawater to explain the biodegradability of the dispersant as well as dispersed ANS. Two oil degrading cultures, isolated from the surface (meso) and deep sea (cryo) of the Gulf of Mexico, were enriched on ANS crude oil at 25 °C (meso) and 5 °C (cryo) were used as inocula. Time series concentrations for oil components (alkanes and aromatics) and an anionic surfactant in Finasol were determined. Results indicated that almost all the surfactant was biodegraded by meso culture, while remained at the lower temperature. Over 90% of the total alkane fraction was biodegraded for the oil with and without dispersant at both the temperatures. For the aromatic fraction, the cryo culture metabolized 76% of the aromatics in ANS alone and 64% in ANS dispersed with Finasol, whereas aromatics persisted in both oil alone and dispersed oil samples at 25 °C. The obtained results figured the effect of dispersant on the fate of spilled oil and rates of oil and dispersant biodegradation, which will be essential for dispersant usage.

Keywords: biodegradation, oil spills, Finasol OSR 52, ANS crude oil

Biodegradability of Dispersed Heavy Fuel Oil at 5 and 25 °C

Mobing Zhuang[1], Gulizhaer Abulikemu[2], Pablo Campo[1],
Makram Suidan[3*], Albert D. Venosa (retired)[4], and Robyn N. Conmy[4]

1. Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, 2901 Woodside Drive, Cincinnati, OH 45221, USA
2. Pegasus Technical Services Inc., 46 E Hollister St, Cincinnati, OH 45219 USA
3. Faculty of Engineering and Architecture, American University of Beirut, Bechtel Engineering Bldg. - 3rd flr. - Room 308 P.O. Box: 11-0236 Riad El Solh 1107 2020, Beirut, Lebanon
4. U.S. Environmental Protection Agency, National Risk Management Risk Laboratory, 26 W. MLK Drive Cincinnati, OH, 45268, USA

Abstract

Fuel oil is produced by blending heavy residual oils with a lighter oil to meet specifications for viscosity and pour point. Compare to lighter oils, the high density and viscosity of fuel oil make it less susceptible to dispersion and biodegradation. Hence, heavy fuel oil spills could cause more serious damages to the environment and be more difficult to clean. The environmental impacts include coating of wildlife dwelling on water surface, depleting oxygen in the receiving environment, exposing toxic substance to aquatic species, and sediment contamination. Laboratory experiments were conducted to study the biodegradability of Intermediate Fuel Oil 120 (IFO-120) dispersed by Corexit 9500 (C9500) at 5 and 25 °C. The biodegradability of alkanes and aromatics in IFO-120 at both temperatures was studied in the presence and absence of dispersant. When compared with IFO-120 alone treatments, date indicated that the depletion rate of alkanes at both temperatures was unaffected by the presence of dispersant. Conversely, C9500 significantly improved the aromatics uptake as its presence shortened the lag phase at 25 °C from 4 to 2 days and increased their removal extent from 71 to 82%. At 5 °C, the addition of C9500 also improved the overall removal from 70 to 85%. Such enhancement effect could be explained by the promoting of dissolution of soluble aromatics in the presence of surfactants.

Keywords: Heavy fuel oil, C9500, surfactant, oil spills

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Raghuraman Venkatapathy[raghuraman.venkatapathy@ptsied.com]
From: Campo-Moreno, Pablo (campomp)
Sent: Thur 4/23/2015 4:14:24 PM
Subject: Re: biodegradation and jorge sample question

Yep. We're currently collecting samples from the experiment with oil and Finasol at low concentration and will do with dilbit too.
Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
Fax: (513)-556-4162
campomp@ucmail.uc.edu

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.
The adventures for Sherlock Holmes

On Apr 23, 2015, at 11:12 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Whew! I woke up in the middle of the night in a panic about this. Thankfully the issue is resolved. Are / will you be setting aside samples for Jorge from the dilbit biodegration?

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

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conmy.robyn@epa.gov

From: Campo-Moreno, Pablo (campomp) [mailto:campomp@UCMAIL.UC.EDU]
Sent: Thursday, April 23, 2015 10:16 AM
To: Conmy, Robyn
Cc: Raghuraman Venkatapathy
Subject: Re: biodegradation and jorge sample question

Robyn,

So far, the only samples sent to Jorge are from the experiments we ran with low concentrations of oil and C9500 and the two cultures from GOM, so all of them are ok. Jorge and Steve Techtmann at UTK are getting very good results. Steve is studying relationship between the microbial communities and our chemistry data.

Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
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campomp@ucmail.uc.edu

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On Apr 23, 2015, at 9:42 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

It just occurred to me that the new discovery about the pH issues during the biodegradation experiments would mean that the samples that were given to Jorge for sequencing would be bad too. True, correct? I recall that the samples given to him were from the same experiments where the cultures died and no degradation was observed. Please let me know where we stand on this, as we will need to stop sequencing analysis for the moment if this is correct.

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

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conmy.robyn@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Venkatapathy, Raghuraman[Venkatapathy.Raghuraman@epa.gov]
From: Holder, Edith
Sent: Tue 9/1/2015 10:37:23 PM
Subject: data: BFT on Endicott
Ref_oils_BFT.xlsx
bft_ref.pptx

Enclosed is a spreadsheet with a summary table and Student t-tests and a Powerpoint file with graphs.

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Holder, Edith[holder.edith@epa.gov];
raghuraman.venkatapathy@ptsied.com[raghuraman.venkatapathy@ptsied.com]
From: Venkatapathy, Raghuraman
Sent: Fri 9/11/2015 3:18:33 PM
Subject: FW: 2016 GOMRI abstracts
Solidifier_Abstract 2016 GOMRI.docx
Dilbit-Abstract_2016 GOMRI.docx
FINASOL_Abstract_2016 GOMRI.docx
IFO120_Abstract_2016 GOMRI.docx

Hi Robyn,

The abstracts prepared by UC are attached.

Thanks,

raghu

Raghuraman Venkatapathy
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Sent: Thursday, September 10, 2015 17:35
To: Raghu Venkatapathy
Subject: 2016 GOMRI abstracts

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Regards,

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Research Assistant Professor
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campomp@ucmail.uc.edu

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The adventures for Sherlock Holmes

Biodegradation of Finasol OSR 52 and Dispersed Alaska North Slope Crude Oil at 5 °C and 25 °C

Yu Zhang[1], Pablo Campo[1],
Ruta Suresh Deshpande[1], Mobing Zhuang[1], and Robyn N. Conmy[2]

1. Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, 2901 Woodside Drive, Cincinnati, OH 45221, USA

2. U.S. Environmental Protection Agency, National Risk Management Risk Laboratory, 26 W. MLK Drive Cincinnati, OH, 45268, USA

Abstract

A study was conducted with Finasol OSR 52 dispersant and Alaska North Slope (ANS) crude oil in sterile GP2 artificial seawater to explain the biodegradability of the dispersant as well as dispersed ANS. Two oil degrading cultures, isolated from the surface (meso) and deep sea (cryo) of the Gulf of Mexico, were enriched on ANS crude oil at 25 °C (meso) and 5 °C (cryo) were used as inocula. Time series concentrations for oil components (alkanes and aromatics) and an anionic surfactant in Finasol were determined. Results indicated that almost all the surfactant was biodegraded by meso culture, while remained at the lower temperature. Over 90% of the total alkane fraction was biodegraded for the oil with and without dispersant at both the temperatures. For the aromatic fraction, the cryo culture metabolized 76% of the aromatics in ANS alone and 64% in ANS dispersed with Finasol, whereas aromatics persisted in both oil alone and dispersed oil samples at 25 °C. The obtained results figured the effect of dispersant on the fate of spilled oil and rates of oil and dispersant biodegradation, which will be essential for dispersant usage.

Keywords: biodegradation, oil spills, Finasol OSR 52, ANS crude oil

Biodegradability of Dispersed Heavy Fuel Oil at 5 and 25 °C

Mobing Zhuang[1], Gulizhaer Abulikemu[2], Pablo Campo[1],
Makram Suidan[3*], Albert D. Venosa (retired)[4], and Robyn N. Conmy[4]

1. Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, 2901 Woodside Drive, Cincinnati, OH 45221, USA
2. Pegasus Technical Services Inc., 46 E Hollister St, Cincinnati, OH 45219 USA
3. Faculty of Engineering and Architecture, American University of Beirut, Bechtel Engineering Bldg. - 3rd flr. - Room 308 P.O. Box: 11-0236 Riad El Solh 1107 2020, Beirut, Lebanon
4. U.S. Environmental Protection Agency, National Risk Management Risk Laboratory, 26 W. MLK Drive Cincinnati, OH, 45268, USA

Abstract

Fuel oil is produced by blending heavy residual oils with a lighter oil to meet specifications for viscosity and pour point. Compare to lighter oils, the high density and viscosity of fuel oil make it less susceptible to dispersion and biodegradation. Hence, heavy fuel oil spills could cause more serious damages to the environment and be more difficult to clean. The environmental impacts include coating of wildlife dwelling on water surface, depleting oxygen in the receiving environment, exposing toxic substance to aquatic species, and sediment contamination. Laboratory experiments were conducted to study the biodegradability of Intermediate Fuel Oil 120 (IFO-120) dispersed by Corexit 9500 (C9500) at 5 and 25 °C. The biodegradability of alkanes and aromatics in IFO-120 at both temperatures was studied in the presence and absence of dispersant. When compared with IFO-120 alone treatments, date indicated that the depletion rate of alkanes at both temperatures was unaffected by the presence of dispersant. Conversely, C9500 significantly improved the aromatics uptake as its presence shortened the lag phase at 25 °C from 4 to 2 days and increased their removal extent from 71 to 82%. At 5 °C, the addition of C9500 also improved the overall removal from 70 to 85%. Such enhancement effect could be explained by the promoting of dissolution of soluble aromatics in the presence of surfactants.

Keywords: Heavy fuel oil, C9500, surfactant, oil spills

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Wilson, Gregory
Sent: Wed 5/13/2015 5:37:37 PM
Subject: FW: IMO Subsea Dispersant Table of Contents (Outline)
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IMO-Manual.pdf
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fyi

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Sent: Wednesday, May 13, 2015 1:32 PM
To: 'john.caplis@bsee.gov'; 'timothy.steffek@bsee.gov'; 'carl.childs@noaa.gov'; michael.k.sams@uscg.mil; Lundgren, Scott; Faulkner, Mike; Principe, Vanessa; Tulis, Dana; Matthiessen, Craig; Wilson, Gregory; DeHaven, Leigh; Jozsef, Aaron L LT; brwalker@fs.fed.us
Subject: IMO Subsea Dispersant Table of Contents (Outline)

(Switch to HTML)

Good afternoon,

Agenda is attached. The call-in number is on the agenda and below. I had some issues with utilizing the drop-box tool for the references last night, but should have it rectified soon. With that said, attached is a new reference from IPIECA which should be useful for multiple sections.

To facilitate the discussion this afternoon, below is a draft outline of the subsea dispersant topic with some initial ideas of topic leads for each section. Knowing that each of you have expertise in each subject, the outline below is open to whichever section(s) you feel you could best contribute. The meeting will be relatively short as we are only looking for section leads at this point with an understanding that section titles/topics may change as more thought is poured into each section.

1. Intro (**LT Aten, Mr. Lundgren**)

•□□□□□□□□ Describe the role of subsea dispersion within the overall strategy of a response to a subsea oil release.

2. Role in Response Strategies/Conditions for Use **(EPA / NOAA / USCG)**

•□□□□□□□□ Advantages/disadvantages/conditions when Sub Sea dispersion is advisable as opposed or in addition to other response strategies? Would it include discussion of physical/chemical/mechanism of action?

•□□□□□□□□ General discussion of the advantages and disadvantages of using subsea dispersants, and under what type of conditions it might be a suitable response option to implement

3. Decision-Making Procedures **(EPA / USCG / NOAA / BSEE)?**

•□□□□□□□□ Tradeoff assessment considered to inform the determination to use this strategy, and as part of the authorization request process? Not sure that "conditions of use" would not be part of the authorization process, which I understand would establish use parameters on a case-by-case basis.

•□□□□□□□□ There could be a discussion on the concepts involved with the process of decision-making and approval, including pre-incident planning, decision-making for initial dispersant usage, and for continued day-to-day operational decision-making as new information is presented (ie results of monitoring, etc). I would mention NEBA as a process that should be used to inform decision-making at all three steps, but I would not try to address the details of the various conditions that would be considered in the NEBA (probably too much detail).

4. Operations **(BSEE / USCG)**

•□□□□□□□□ Describe the main features of the various specialized equipment available in the

world today as well as the logistical requirements related to mobilization and deployment of this equipment;

5. Monitoring **(EPA / USDA / NOAA / BSEE)**

•□□□□□□□□ Describe methodologies for operational monitoring and control of a subsea dispersion operation;

6. **Fate and Effects? (EPA / NOAA / USDA)**

7. Data and Information Management **(USCG / EPA)**

•□□□□□□□□ Internal and external communications

Number: (877) 950-0401

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Very Respectfully,

LT Brandon Aten

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IMO SUBSEA DISPERSANT CHAPTER DEVELOPMENT MEETING

TELECONFERENCE AGENDA

WEDNESDAY, MAY 13TH, 2015
1500 – 1530 (EASTERN)

NUMBER: (877) 950-0401
PARTICIPANT CODE: 5627627
ROOM: 6T06-02 (CGHQ)

I. Kick Off and Roll Call – LT Brandon Aten (1500)

II. Mr. Lundgren Opening Remarks – (1505)

III. IMO Subsea Dispersant Chapter Assignments (1505-1520)
- **Review Current Outline**
- **Assign team members to appropriate chapters**
- **IMO writing/stylistic expectations**

IV. Schedule Next Meeting and Closing Comments (1525-1530)
- In Progress Review Meeting: Wednesday, June 3rd at 1500-1530 (Eastern)

IPIECA

International Association of Oil & Gas Producers

Dispersants: Subsea Use
(Subsea Dispersant Injection: SSDI)

Principles, experience and the operational aspects of subsea use

IPIECA

The global oil and gas industry association for environmental and social issues

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Dispersants: Subsea Use (Subsea Dispersant Injection: SSDI)

Principles, experience and the operational aspects of subsea use

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Executive summary

The reason for using dispersants, either on floating oil or by subsea use, is the same; to minimize the overall ecological and socio-economic damage, by preventing the released oil from drifting into nearshore or coastal habitats and onto the shore. Dispersant use on floating oil transfers the oil from the sea surface and into the upper layer of the water column. Subsea dispersant use aims to prevent the oil released subsea from reaching the sea surface by dispersing the oil into the water close to the release. This provides a major health and safety benefit by greatly reducing the exposure of personnel responding near the release site to volatile organic compounds (VOCs). Adding dispersant to the released oil and gas subsea causes a greater proportion of the released oil to be produced as small oil droplets that will be retained in the water column, unlike the larger oil droplets that will float up to the sea surface. The surfactants in the dispersant greatly reduce the oil / water interfacial tension that exists between oil and water and this permits the intense turbulence associated with a subsea oil and gas release to convert a greater proportion of the released oil into small oil droplets.

The experience gained during the response to the uncontrolled release from Macondo well associated with the *Deepwater Horizon* incident in 2010 has shown that subsea dispersant injection (SSDI) can be an effective response technique for subsea oil and gas blowouts. More oil would have come ashore if subsea dispersant use had not been undertaken. The challenges of conducting a response to oil released 5,100 feet (1,550 m) below the sea surface with a technique that had never been used before were great. Considerable ingenuity and expertise were required to develop SSDI into a viable response during the largest oil spill response ever conducted.

As a subsea response to a subsea oil release, SSDI has many advantages over the strategy of responding to the released oil only when it reaches the sea surface. Using SSDI:

- Treats all the oil released at the point of release;
- Less dispersant is required compared to surface treatment;
- Reduces the exposure of responders to the health and safety hazards of volatile organic compounds (VOCs) and oil;
- Operations can be conducted continuously, day and night and in practically any weather conditions, unlike response techniques on the sea surface.

Dispersing released oil into the water column has capabilities and limitations plus potential benefits and risks that, like the consideration of any response technique, need to be addressed by conducting NEBA (Net Environmental Benefit Analysis). The addition of dispersant will cause more of the released oil to be produced as the smaller oil droplets that will be retained within the water column. SSDI use has benefits:

- Dispersing the released oil into the water column prevents the oil from reaching the sea surface from where it could drift inshore causing severe and long-lasting damage to oil-sensitive coastal habitats and socio-economic resources.
- Dispersing the oil into the water as small oil droplets permits rapid colonization by petroleum-degrading microorganisms that naturally occur in ocean environments. These microorganisms will substantially biodegrade the majority of the oil within days and weeks. The dispersant will also be biodegraded.

However, increasing the amount and concentrations of dispersed oil in the water increases the risk to marine organisms of toxic effects caused by exposure to dispersed oil, but only from the already high exposure levels that will occur at high-energy oil and gas blowouts. The trade-offs involved in using SSDI need to be understood by all concerned and, ideally, should be addressed during contingency planning.

The logistics of conducting SSDI require considerable specialist equipment, trained personnel and support. Multiple ROVs will be required with dedicated offshore supply vessels and a logistical supply chain for dispersant stocks.

Subsea dispersant use requires subsea monitoring to assess whether it is being effective and where the subsea plumes of oil would be transported by the prevailing deep water currents. In order to address concerns about the possibility of toxic effects being caused to marine organisms by the dispersed oil, it may be necessary to conduct extensive water monitoring and water-sampling surveys with subsequent chemical analysis to ensure that oil concentrations and oil extent do not

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exceed assumptions made in a NEBA analysis for the event. This was done during the *Deepwater Horizon* incident. The results showed that concerns about substantial toxic effects to marine organisms, oxygen depletion in the water due to biodegradation and the persistence of dispersant in the water column were not borne out by the measurements made.

Part One: Principles

Role of dispersant use in oil spill response

The use of oil spill dispersants is one of several possible at-sea response techniques. Dispersant application can be a useful way of minimizing safety risks at a release site and reducing an incident's overall damage by removing oil from the sea's surface by transferring it into the water column, preventing it from reaching sensitive coastal habitats and shorelines. Dispersion of oil enhances the natural biodegradation processes that break down oil. Dispersant use does not sink the oil to the seabed.

Like all techniques in the response toolkit, dispersant use has some limitations, but also has capabilities that make it particularly useful in responding to larger oil spills at sea. A companion IPIECA Good Practice Guide (GPG) entitled "Dispersants: Surface Application" (IPIECA, 2015a) describes the use of dispersant in responding to floating oil. This GPG specifically deals with the use of dispersants in responding to subsea oil releases.

During the release of oil and gas from the Macondo well associated with the *Deepwater Horizon* incident in 2010, subsea dispersant injection (SSDI) was used for the first time to treat the oil with dispersant directly at the source of a large scale blow-out event. This was a novel way to apply dispersants and is described in some detail in this GPG.

The reason for using SSDI at a subsea oil release is the same as for any dispersant use; to prevent, or minimize the amount of, the oil from subsequently drifting into shallow coastal waters or onto the shore, where it could cause considerable damage to habitats and species present and disrupt socio-economic activities. Any successful dispersant use involves transferring more oil into the water column than would otherwise be the case.

- Dispersant use on floating oil transfers oil from the sea surface and into the upper layer of the water column.
- SSDI increases the proportion of oil that is retained in the water column, compared to that which reaches the sea surface and could drift ashore.

Subsea dispersant use is a response to a subsea oil release. It is therefore convenient to first consider how oil released subsea can behave.

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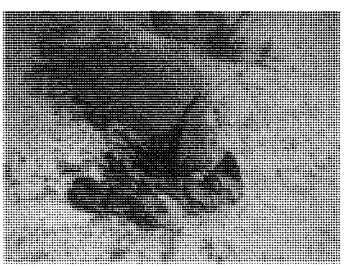
Behavio ur of oil released subsea

Oil can be released subsea in a number of ways, including:

- Subsea blowouts, for example the Macondo well at the *Deepwater Horizon* incident in 2010 and the *Ixtoc 1* incident in 1979 (Farringdon, 1980).
- Seabed fissure, for example the Frade Field seep in Brazil's Campos Basin in 2012 (Chevron, 2012) and other widespread natural seeps throughout the world's oceans.
- Subsea flowline (the pipes connecting subsea wells to the offshore installation) leaks or ruptures; and
- Subsea oil export pipeline leaks or ruptures.
- From fuel or cargo tanks of sunken vessels.

The behaviour of the oil released will be the result of the:

- Characteristics of the release:
  The oil and gas pressures and flow rates, Gas Oil Ratio (GOR), the size and geometry of the release.
- Water conditions into which the oil is released:
  The water depth (therefore hydrostatic pressure), temperature and the currents and the oceanographic conditions at the release site
- The properties of the oil that was released:
  In most cases, the oil released at a subsea blowout will be at high temperature, but will be rapidly chilled when it comes into contact with the cold seawater in deep water. The density, viscosity and pour point of the oil - and how these oil properties change with time - will influence the behaviour of the released oil.



Natural low-pressure seep off the Californian coast (credit USGS)

The principle characteristic of oil released subsea that controls the subsequent behavio ur is the size, or size distribution, of the oil droplets that are produced:

- High-pressure, high-velocity oil releases, particularly with a gas phase present, will produce small oil droplets and gas bubbles in the water. The subsequent behavio ur of the oil and gas will depend on water depth.
- Low-pressure, slow releases without gas present will allow the oil to enter the water as large globules.

The speed that an oil droplet will rise through static seawater (salinity of 32 ‰ i.e. density of 1.024 g/ml) is dependent on the oil density and droplet size. Almost all crude oils are less dense than seawater so will tend to float, but large oil droplets float towards the sea surface much more rapidly than smaller oil droplets (Table X, which does not consider the effect of biodegradation of oil droplets). Smaller oil droplets will be biodegraded long before they could reach the sea surface.

Oil droplet diameter (oil density = 0.85)	Time to rise 1 metre	Time to rise 1,500 metres
4 mm (4,000 µm)	3 to 5 sec	1 to 2 hours
3 mm (3,000 µm)	5 to 10 sec	2 to 4 hours
2 mm (2,000 µm)	About 15 sec	About 6 hours
1 mm (1,000 µm)	About 20 sec	About 8 hours
0.4 mm (400 µm)	85 sec	35 hours
0.2 mm (200 µm)	5 min	5 days
0.1 mm (100 µm)	19 min	20 days
0.05 mm (50 µm)	1.3 hours	80 days
0.02 mm (20 µm)	8 hours	1.4 years
0.01mm (10 µm)	31 hours	5.4 years

Table X. Oil droplet diameter and rise times through static seawater (Oil droplets larger than 0.4 mm in diameter deform from a spherical shape during a rapid ascent through water and time estimate become less accurate)

Subsea blowout

Theoretical studies of what could happen to oil released at subsea blowouts in deep water have been made, but only one large-scale field experiment had been conducted to either confirm or modify the theoretical considerations.

This was the *DeepSpill* experiment conducted in the Norwegian Sea in 2000 in 844 m (2,770 feet) of water roughly 125 km off the coast of central Norway (Johansen et al., 2001 and Johansen et al, 2003) Four controlled discharges of oil and gas were made amounting to a total of 120 m^3 (755 bbl) of oil and 10,000 standard m^3 of natural gas. This experiment only studied untreated oil and no dispersant were used. Extensive observations were made of wind, currents, water density, surface and subsurface oil concentrations, and chemical and biological samples in the water column. The oil started reaching the surface about an hour after the release began and within a few hundred meters of the release site. Oil continued to surface for several hours after the release stopped. No gas hydrates were formed. No gas bubbles reached the sea surface indicating that the gas had dissolved into the water. The echo sounders on-board the research vessels were able to track the oil/gas plume as it rose through the water column.

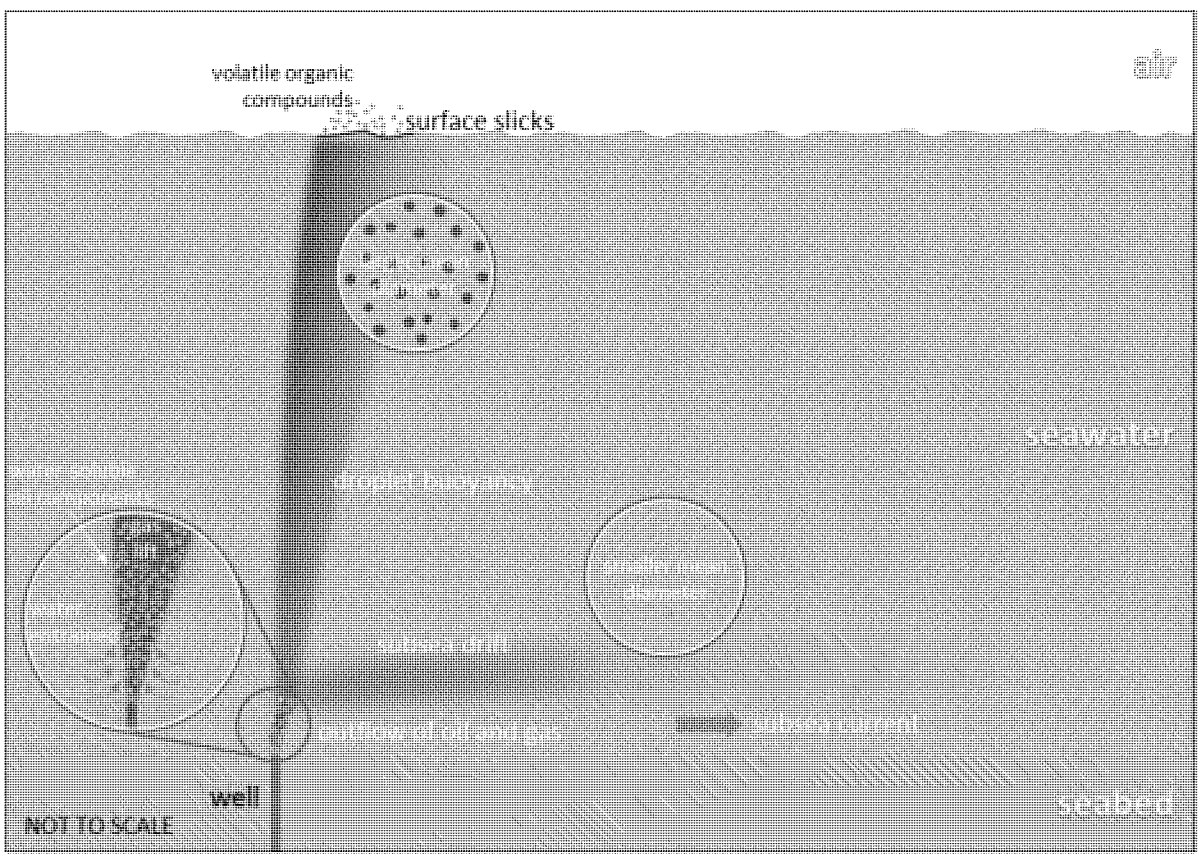


Figure X: Schematic representation of a subsea release

Notes: This diagram is representative of the processes that occurred at DeepSpill experiments and at the Deepwater Horizon incident and is not to scale.

The plume of larger oil droplets that rise to sea surface and the plume of smaller dispersed oil droplets that are stratified horizontally and remain in the water column are visualized in colour in the diagram

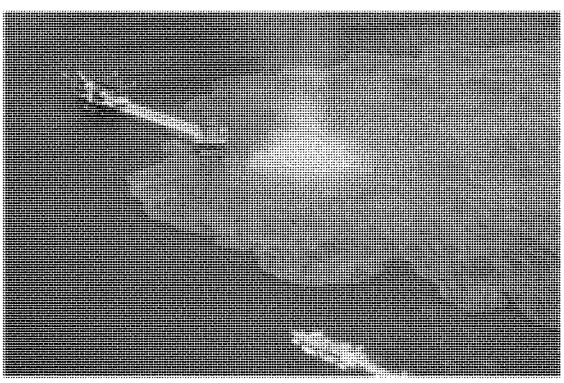
purely as an aid to the explanation. Dispersed oil plumes in the water column are not visible and require sensitive instrumentation to detect them, as the dispersed oil is diluted into the water column

The conclusions of the *DeepSpill* field experiment, two other follow-up laboratory studies and three model comparisons were summarized in a 2005 report entitled Review of *DeepSpill* Modeling Activity Supported by the *DeepSpill* JIP and Offshore Operators Committee (Adams and Socolofsky, 2005). This report indicated that:

- High velocity jets of oil and methane gas released subsea in deep water will be broken up by the intense turbulence of the release conditions into small oil droplets and gas bubbles.
- The plume of small oil droplets, gas bubbles and entrained water will initially rise rapidly in the form of a buoyant plume, with the gas providing the dominant source of lift and buoyancy. Close to the point of release, this plume will behave like a single phase plume.
- As the plume of oil droplets and gas bubbles rise through the deep water (more than 500 m in depth), the methane gas will dissolve into the sea (due to its solubility at high pressure); this reduces the buoyancy of the plume, thereby slowing its ascent through the water.
- Stratification in the water column and currents will the separate the oil droplets and gas bubbles (if not already dissolved) from the plume of entrained water.
- The larger oil droplets will then continue to slowly rise to the sea surface under their own buoyancy which is a function of size, while the smaller oil droplets will be carried horizontally and remain suspended in the water column.

These processes are schematically represented in Figure X.

Not all of the oil that is released from the subsea blowout in deep water will reach the sea surface. The intense turbulence caused by the high-velocity, high-flow rate jet of oil and gas being released into the water will convert a proportion of the released oil volume into oil droplets that are small enough to be retained in the water column by the prevailing currents in the stratified water column. The proportion of oil that is dispersed by the turbulence of the release will depend on the precise circumstances of the release.



Ixtoc I blowout, Mexico 1979, in water less than 100m deep (credit NOAA)

At oil and gas releases from subsea blowouts in water of less than 500 metres depth, the gas may not totally dissolve into the water. At oil and gas blowouts in more shallow water, the buoyant plume of gas bubbles will rapidly arrive at the sea surface where the gas will escape into the air (with the possibility of a fire / explosion hazards) and the oil will initially spread out radially over the sea surface. The surfaced oil will then be subjected to typical weathering processes including wind- and surface current-driven movement, evaporation, fragmentation and possible emulsification.

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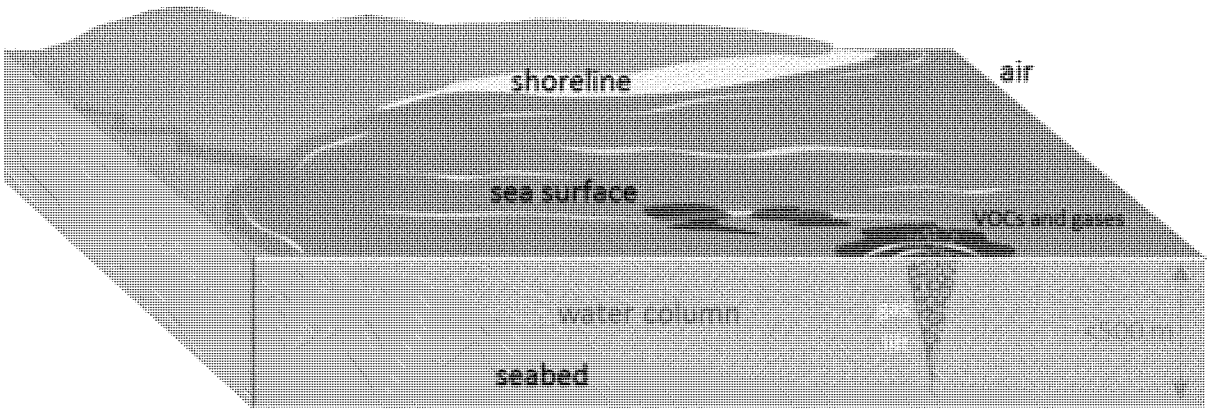

Schematic representation of a shallow water oil and gas blowout with the majority of the released gas reaching the surface (not to scale)

Other subsea releases

The circumstances of each subsea oil release needs to be considered when assessing the probable outcome. Several computer models are available to forecast the likely oil behaviour.

- A pinhole leak in a subsea flowline carrying oil and gas will result in a fine jet of small oil droplets entering the water, but the released oil volume will be low. A rupture of such a flowline will result in an initially rapid discharge of oil and gas, but this will cease as the flowline is isolated and the line depressurizes.

- The rupture of a subsea oil export pipeline after the gas has been removed by processing offshore, will cause an initially rapid displacement of the oil into the water, followed by a much slower release of oil as the ruptured pipeline fills with water. The oil will rise as large globules.

- Releases from sunken vessels would depend on the circumstances but are likely to be slow and result in large globules of fuel or cargo oil.

Potential consequences of oil released subsea

As described in the previous section, all of the oil released from a subsea blowout will enter the water column in the form of oil droplets of a variety of sizes produced by the turbulence associated with the subsea oil and gas release. Relatively large oil droplets will rise relatively rapidly through the water column, but smaller oil droplets will rise much more slowly and some will be retained in the water column.

Potential for effects in the water column

The potential risk is of toxic effects being caused to marine organisms in the water column by exposure to the plumes of dispersed oil droplets and the water-soluble oil compounds that will be released from the oil droplets. Adult fish can detect oil compounds in the water and are likely to move away to avoid the contaminated area, while plankton drift with the currents and cannot avoid exposure to the compounds from the oil.

The exposure is of limited duration from the larger oil droplets that float upwards and eventually arrive at the sea surface. The exposure duration to organisms in deeper water will be more prolonged in the case of the plumes of smaller oil droplets that are retained in the water column by the stratified water layers. However dilution will occur quite rapidly as the plume is carried by subsea currents.

Potential for effects on the sea surface

Released oil rising to the sea surface will spread out and form oil slicks in the vicinity of the release. The more volatile components of the oil (Benzene, Toluene, Ethylbenzene and Xylenes, often collectively referred to as volatile organic compounds or VOCs), that have not already dissolved into the water, will either dissolve in the water or evaporate from the oil and into the air. This could pose health and safety concerns for responders.

Floating oil will drift under the influence of the prevailing wind and currents. The potential risks of oil drifting on the sea surface are that seabirds will be contaminated with oil, leading to toxic effects or hypothermia, and to marine mammals at the sea surface. In addition, any organism that reside in the water column near the sea surface will be impacted by the oil. Many fish eggs and larva tend to float near the surface. Any of these sensitive life stages that encounter surface oil will be impacted.

The most oil-sensitive ecological resources are most often those in coastal waters or on shorelines. These nearshore areas are also the breeding grounds of many species of fish and invertebrates. Oil drifting towards the shore could come into contact with these ecological resources and also disrupt important coastal socio-economic activities.

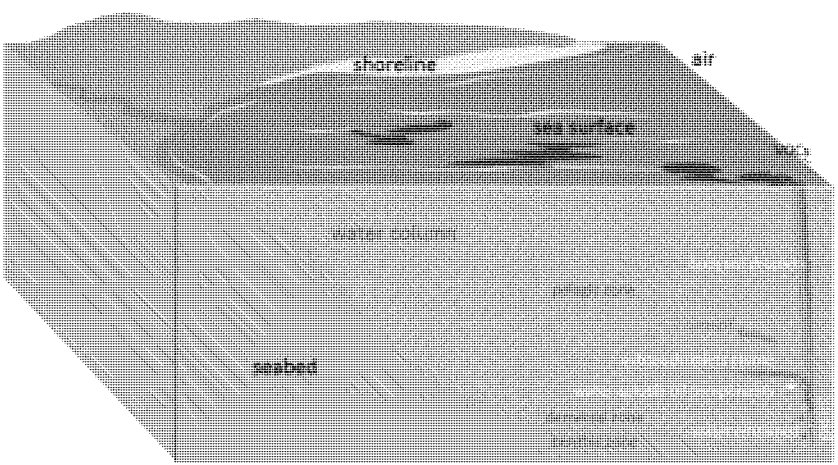

Figure X: Schematic representation of the environmental compartments in relation to a subsea release in deeper waters Note: Dispersed oil plumes in the water column are not visible and require sensitive instrumentation to detect them, as the dispersed oil is diluted into the water column

Oil spilled at sea has the potential to cause negative effects to a variety of ecological and socio-economic resources, depending on the environment compartment it is in. These are summarized in Figure X and Table X. Further information is provided in the IPIECA-OGP Marine Ecology and Shoreline Ecology Good Practice Guides.

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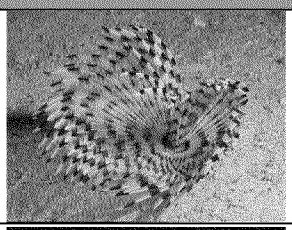
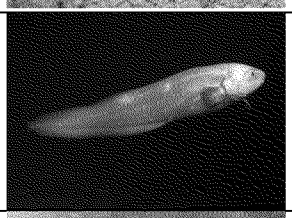
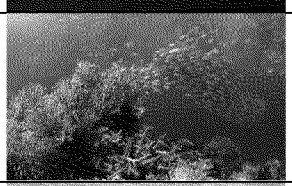
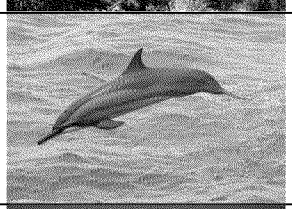
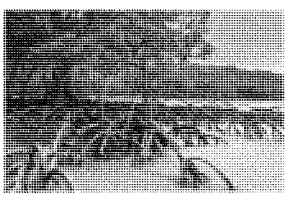
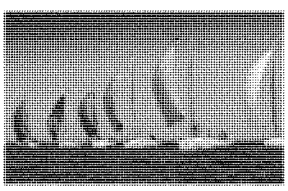
Environmental compartment			Potential effects of oil
Seabed benthic zone			Subsea dispersed oil will either float to the surface or form part of underwater plumes that dilute and biodegrade as they move from the source of the release. The majority of the oil present as small oil droplets in the water will be biodegraded within days or weeks. The oil compounds that are resistant to biodegradation, often referred to as being the 'recalcitrant residue', are similar to those in bitumen or asphalt and are largely biologically inert and of low toxicity. The recalcitrant residue will be present at very low concentrations of a few ppb (parts per billion) in water as the remnants of the biodegraded dispersed oil droplets. This recalcitrant oil residue will eventually be deposited over the seabed at extremely low concentrations over a very large area.
Water column	Near seabed demersal zone		
	Deep water pelagic		Animals living in deep open waters may be exposed to mechanically dispersed oil plumes. Potentially harmful concentration would be limited to the release site. Free swimming fish would be likely to detect and avoid areas of high oil concentration.
	Nearshore		Shallow nearshore habitats such as coral reefs are susceptible to damage by naturally dispersed oil exposure. Reefs more than 10m deep are at low risk of harmful concentration of oil due to dilution potential.
Sea surface			Spilled oil floating on the sea surface poses risks to ecological resources such as seabirds, marine mammals and fish eggs/larvae present in the uppermost water column. Floating oil may persistent and serve as long-term source of hydrocarbon contamination in the upper water column.
Nearshore sediments			Naturally dispersed oil droplets that become incorporated into near-shore sediments can result in long-term exposure to the organisms that inhabit the mud and sediment.
Shoreline			Spilled oil on the sea surface will often drift into shallow water and may contaminate coastal habitats including particularly oil-sensitive mud-flats and wetlands. Photos or video of distressed and dying seabirds covered in oil that washed ashore are stark images of the effects of oil spills. Spilled oil can smother shoreline organisms and impact the coastal breeding grounds and juvenile life stages of fish – even those that live offshore as adults. Oil trapped in shoreline substrates can be a source of long-term exposure to shoreline organisms and can be the cause of long-term toxic effects.
Socio-economic			Oil on the sea surface or being released into the sea will likely result in the relevant authorities imposing a fishing ban, thus impacting the livelihoods of fishermen. Water recreation activities can be either prevented or disrupted by oil on the sea surface. Spilled oil drifting onto a tourist beach will render it unusable and this can have an impact on the income of those whose livelihoods depend on tourism. Shoreline economic features such as sea-water intakes or ports and harbours can also be severely disrupted by oil drifting ashore.

Table x: Potential oil effects on environmental compartments

Response to subsea oil releases

Deployment of any technique in the oil spill response toolkit should aim to minimize the damage that could be caused by spilled oil if no response were undertaken. The primary ecological threat from floating oil is considered to be when oil enters the nearshore or comes ashore. Shoreline environments are often more sensitive to oil than open water environments, with the exception of coral reefs, and keeping oil from drifting inshore is often key to minimizing the environmental impacts of an offshore oil spill.

The response to subsea oil releases could be undertaken:

- At the source
  Source control aims to stop the release or prevent the released oil from reaching the sea surface by either subsea containment (with transfer to a surface recovery vessel) or enhancing dispersion of the oil.
- On the sea surface
  After the oil released subsea has risen to the sea surface, where the primary aim of the response is to prevent the oil from drifting ashore.

An advantage of conducting a subsea response is that operations can be undertaken at a known and fixed location, as compared to the oil being present as fragmented patches scattered over a large area of the sea's surface and drifting under the influence of the prevailing wind and currents.

Subsea response

Source control

Stopping the oil from being released subsea will always be the primary focus for response at such incidents. In the case of leaks or ruptures of subsea flowlines or oil export pipelines, there will often be engineering controls that can rapidly shut down the pipeline or isolate the section that has been damaged. Stopping the flow from a subsea blowout where the blow-out preventer (BOP) has failed is a much greater challenge. Drilling relief wells to intercept and divert the oil flow far below the seabed well-head will eventually be effective, but can take weeks to complete. Rapidly-deployable capping stacks to seal off an oil well in the unlikely event of the failure of all safety barriers, including the BOP, have been developed in recent years. The Marine Well Containment Company, the Subsea Well Intervention Service, and other providers now have capping stacks that can be rapidly deployed to all oil exploration, development, and production regions.

Subsea containment and recovery

Recovery of some or all of the oil from the subsea release may be possible by the deployment of various subsea oil collection and recovery devices. After the *Deepwater Horizon* and other incidents, the oil industry's Subsea Well Response Project (SWRP) and the Marine Spill Response Corporation have developed toolkits of containment equipment and subsea well containment guidelines. Services are now available through the Subsea Well Intervention Service (SWIS) and other providers. The containment concept relies on existing drilling rigs and commercially-available well-testing equipment to capture fluids from an incident well and flow them to the surface for processing and disposal. If well-shut in is not possible, the subsea well containment toolkit can be deployed to enable the flow of well hydrocarbons from the capping stack to an offloading tanker.

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Subsea Dispersant Injection (SSDI)

Subsea Dispersant Injection (SSDI) can prevent oil from reaching the sea surface and subsequently drifting ashore. Further information is provide in subsequent sections.

Response to oil on the sea surface

The response techniques available for responding to oil on the sea surface are well-established:

- Mechanical containment of spilled oil with floating barriers (booms) and collection using recovery devices (skimmers):
  Recovered oil is collected in a vessel's tanks or other floating storage for subsequent offloading and either processing or disposal.
- Controlled (or in-situ) burning:
  Oil is corralled in fire-resistant booms and ignited. In situ burning converts the floating oil into airborne combustion products (primarily as carbon dioxide and water vapour with small amounts of soot and other gases) which are rapidly diluted in the atmosphere.
- Dispersant use:
  Transfers the floating oil into the upper layer of the water column as small droplets. The dispersed oil is rapidly diluted to low concentrations in the water. The majority of the oil in these droplets will subsequently be biodegraded by hydrocarbon-degrading organisms. The ultimate fate of most of the oil is to be biologically converted to carbon dioxide and water.

Each of these response techniques has capabilities and limitations that make it more or less suitable for response in specific conditions.

Factor	Containment and recovery	Controlled (in-situ) burning	Dispersant use
Rate at which spilled oil can be encountered	Low	Low	High
Spilled oil removal rate	Low	High during burn	High
Limiting prevailing conditions	Possible up to wind speed of 20 knots and wave height of 1 to 1.8 metres	Possible up to wind speed of 10 knots and wave height of 0.6 to 1 metres	Possible up to wind speed of 35 knots and wave height of 5 metres
Oil type and properties	Need to match skimmer to changing viscosity	Oils that have lost lighter fractions and emulsified oils difficult to ignite	High viscosity oil may be challenging to disperse plus possible pour point limitation

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Dispersants and how they work

Composition of modern dispersants

Dispersants are blends of surfactant in solvents.

Surfactants

Surfactants are surface active substances with numerous domestic and industrial applications. Surfactant molecules have two linked parts; a hydrophilic ('water-loving') part connected to an oleophilic ('oil-loving') part. Surfactants can be classified into various groupings such as anionic (with a negatively charged hydrophilic part), non-ionic (with a non-charged hydrophilic part), cationic (with a positively charged hydrophilic part) or amphoteric (combining cationic and anionic in the same molecule). There are thousands of commercially-available surfactants. They are the active ingredients in many household products such as soaps, shampoos, food additives, cosmetics, cleaners and detergents. No surfactants are manufactured specifically for use in oil spill dispersants.

The function of surfactants in most applications is to the lower the interfacial tension (IFT) between two fluids. Surfactants used in common cleaners reduce the surface tension of the water (also called the air/water IFT) so the water can more effectively wet the fibres and surfaces to be cleaned. They loosen and encapsulate the dirt and this ensures that the dirt will not be re-deposited on the surfaces.

Surfactants used in dispersants reduce the oil/water IFT by becoming orientated at the oil/water interface. The oleophilic part of the surfactant molecule is in the oil and the hydrophilic part is in the water. The surfactant forms a 'bridge' between the oil and water. The interface between the oil and the water is now occupied by the surfactants and this reduces the oil/water IFT by around 30 times if a modern, well-formulated dispersant is used.

Solvents

Solvents used in modern dispersants include glycol ethers, hydrocarbon and water (Fiocco et al., 1995). A solvent is necessary to produce a liquid dispersant that can be easily sprayed. Many surfactants are high viscosity liquids and/or solids, so they need to be blended into a solvent to produce a dispersant of relatively low viscosity. The solvent also allows the dispersant to be positively buoyant and helps the surfactant to penetrate into the spilled oil.

The precise blends / formulations of most dispersants are proprietary information. However, the formulation details may be shared, in confidence, to national regulators as part of the dispersant listing or approval process. Most dispersants consist of a blend of two or three non-ionic surfactants (Brochu et al., 1986) and sometimes include an anionic surfactant (Brandvik and Daling, 1998). All of the surfactants used in dispersants are also used in many other household products.

The ingredients list of the widely stockpiled Corexit® dispersants has been published by their manufacturer, as shown in the table.

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Chemical Abstracts Service number	Name	Generic name	Common Everyday Use Examples
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	Span	Skin cream, body shampoo, emulsifier in juice
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs	Tween	Baby bath, mouth wash, face lotion, emulsifier in food
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs	Tween	Body/Face lotion, tanning lotions
577-11-7	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1) (contains 2-Propanediol)	DOSS	Wetting agent in cosmetic products, gelatin, beverages
29911-28-2	Propanol, 1-(2-butoxy-1-methylethoxy)	Glycol ether solvent	Household cleaning products
64742-47-8	Distillates (petroleum), hydrotreated light	Hydrocarbon solvent	Air freshener, cleaner
111-76-2	Ethanol, 2-butoxy [NOT included in the composition of COREXIT® 9500]	Glycol ether solvent	Cleaners

Some of the most widely used non-ionic surfactants have a hydrophilic part based on sorbitan (derived from sorbitol - a sugar) and an oleophilic part based on a fatty acid (a vegetable oil) (Al-Sabagh et al., 2007). These non-ionic surfactants have the generic trade name of "Spans". Other non-ionic surfactants used are generically known as "Tweens" and these are ethoxylated sorbitan esters. Spans and Tweens have applications in the pharmaceutical, cosmetic, food and agrochemical industries. The anionic surfactant used in many modern dispersants is sodium diiso-octyl sulphosuccinate (sometimes referred to as DOSS). This surfactant is also used in many household products, such as cleaners of various types and health treatment.

Mechanism of dispersant action subsea

Dispersants greatly reduce the IFT that exists between oil and water when they are added to the oil. The surfactants in dispersants 'bridge' the differences between the inherent properties of oil and water. This allows the prevailing mixing energy to produce a much higher proportion of smaller oil droplets when dispersant is added, than when it is not. When dispersant is use on floating oil the prevailing mixing energy is from wave action (see Dispersant: Surface application GPG).

When dispersant is used subsea on a blowout, the prevailing mixing energy is the intense turbulence produced at the point of the oil and gas release. If the oil release is a high-pressure, high-velocity event, particularly with a gas phase present, it will produce a plume of small oil droplets and gas bubbles in the water. The proportion of the released oil volume converted into oil droplets that are small enough to be retained within the water column may already be substantial.

Dispersant that is added subsea to the oil release will cause a large reduction in the IFT and the turbulence of the release conditions will convert a greater proportion of the oil into droplets that are small enough to be retained in the water column by the prevailing oceanographic conditions.

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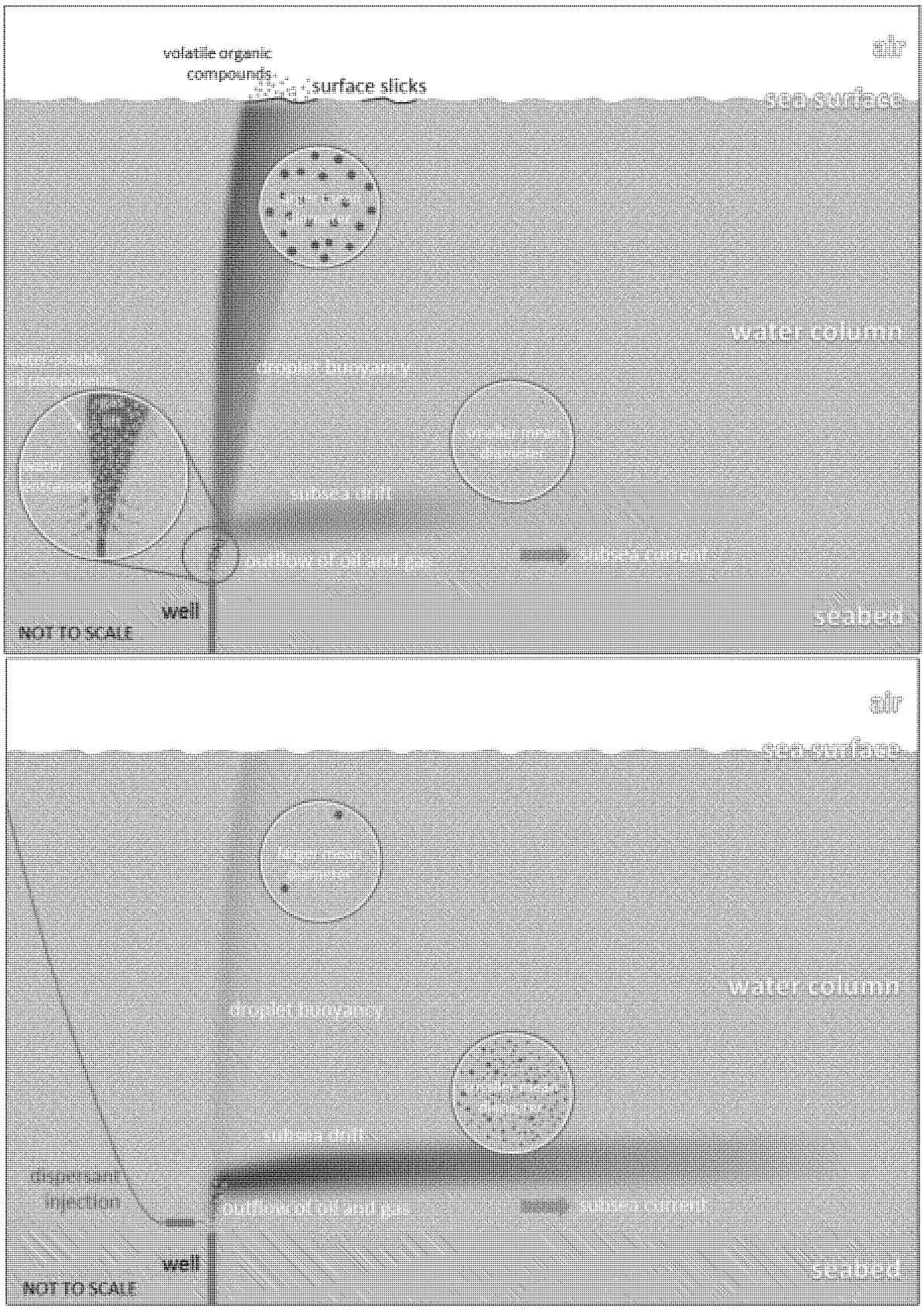

Figure X. Schematic representation of subsea release with (below) and without (above) dispersant addition
Note: Dispersed oil plumes in the water column are not visible and require sensitive instrumentation to detect them, as the dispersed oil is diluted into the water column

Potential benefits and drawbacks of subsea dispersant use

The reason for using SSDI at a subsea blowout is the same as for any dispersant use; to prevent, or minimize, the amount of oil that may subsequently drifting into shallow coastal waters or onto the shore, where it could cause considerable damage to inshore habitats and disrupt socio-economic activities. SSDI also provides a major health and safety benefit by greatly reducing the exposure of personnel responding near the release site to volatile organic compounds (VOCs).

Benefits of dispersant use

The benefits of dispersant use are:

- It minimizes long-term damages and disruption to sensitive wildlife, coastal habitats and socio-economic features that could occur if dispersant were not used and the oil either remained on the surface or reached coastal waters and shorelines.
- It increases the availability of oil for biodegradation and thereby speeds up its natural break-down and assimilation into the environment.
- It can reduce potentially harmful vapours in the vicinity of a spill and provide a safety benefit to any responders undertaking vessel-based activities in the immediate area, as well as minimizing the exposure of responders and local communities to oil in the wider context.
- Reduces the amount of dispersant required compared to surface application and can be operated 24/7.
- The need for potentially large-scale and prolonged shoreline clean-up operations is removed.
- It avoids the creation of large volumes of waste material often associated with shoreline clean-up operations; such waste brings serious environmental challenges during its handling, storage and disposal.

The specific potential benefit of subsea dispersant use is that it can prevent, or minimize, the amount of oil reaching the surface. An efficient subsea dispersant delivery system could potentially treat the vast majority of oil escaping from a single release point before it reaches the surface and forms a widely spread floating slick.

Once deployed, subsea dispersant use will be able to treat the oil released from a point-source with a very high encounter rate, can continue 24/7 and is generally not limited by weather.

Drawbacks of subsea dispersant use

Any successful dispersant use (on the sea surface or subsea) involves transferring more of the oil into the water column than would otherwise be the case. The potential risk of any dispersant use is the increased exposure of marine organisms in the water column to dispersed oil droplets and water-soluble oil compounds released from these oil droplets.

At many subsea oil and gas blowouts, a substantial proportion of the released oil volume may already have been produced in the form of a plume of very small oil droplets in the water by the intense turbulence created by the high-velocity flow of oil and gas into the water. Adding dispersant to the oil being released will increase the proportion of oil dispersed as very small oil droplets.

Evaluating the consequences of subsea dispersant use are further discussed in the context of Net Environmental Benefit Analysis (NEBA).

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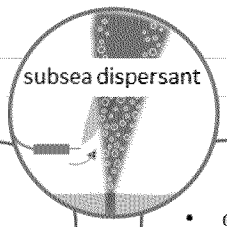

Benefits

- Reduces the volume of surfacing oil and minimizes long-term damages to sensitive wildlife, coastal habitats and socio-economic features
- increases the availability of oil for biodegradation
- It can reduce potentially harmful vapours in the vicinity of a spill
- potentially large-scale and prolonged shoreline clean-up operations is avoided
- creation of large volumes of waste material often associated with shoreline clean-up operations avoided
- very high oil encounter rate
- uses less dispersant and operable under a wide range of weather conditions 24/7

Drawbacks

- does not directly collect oil but rather transfers into the water column
- increases the exposure of marine organisms in the water column to plumes of dispersed oil droplets and water-soluble oil compounds

Capabilities and limitations

The capabilities and limitations of dispersant use on floating oil are described in the "Dispersants: Surface Application" GPG.

Capabilities of subsea dispersant use

All subsea response techniques have the potential capability - once deployed - to deal with all the oil being released from the point-source. This is in contrast to response to floating oil, where the very large area of fragmented and scattered oil on the sea's surface is often a limiting factor. The rate at which any oil response can come into contact with oil is commonly called the encounter rate. The encounter rate of surface response techniques is often very low, while the encounter rate of all subsea response techniques is potentially very high; all of the released oil can be 'encountered' in a very small area, albeit that this limited area may be at some distance below the sea surface.

The potential capability of subsea dispersant use should therefore be initially compared with those of other subsea response techniques such as subsea capping and subsea containment and recovery. The limiting factor common to all these methods is the speed with which the required equipment and personnel can be deployed to the site of the oil release and the capability to conduct the response in the water depth at which the release is occurring.

The logistics involved with transporting bulky, heavy equipment (a capping stack can weigh 300 tonnes) from where it is stored to where it is required can be formidable. Subsea containment and recovery equipment can also be heavy requiring special transportation needs.

Factor	Subsea Capping	Subsea Containment	Subsea Dispersant Injection
Rate at which oil can be encountered	Very high		
Oil treatment rate	Prevents well fluid flow	Captures well fluid	Very high
Deployment factors	Initial debris removal may be required	Applicable in rare scenarios where capping is either not sufficient or not possible	Applicable while capping and containment systems are being deployed
Limitations	Current systems typically limited to maximum of 3,000m water depth and 15,000 psi pressure	Current systems typically limited to maximum of 3,000m water depth	Current systems typically limited to maximum of 3,000m water depth

Limitations of subsea dispersant use

The prevailing sea state and oil properties, principally oil viscosity, and the way that the viscosity increases as spilled oil 'weathers', determine the effectiveness of dispersant use on floating oil.

Subsea dispersant use will not be affected by the prevailing mixing energy provided by wave action at the sea surface or by the change in oil properties as it 'weathers'.

At a subsea blowout, there is a continuous 'supply' of crude oil and gas from the reservoir. Dispersant would be added to the oil as it flows into the water. Although the oil properties will rapidly change due to dissolution of some of the water-soluble compounds in the oil into the water and the sudden drop in

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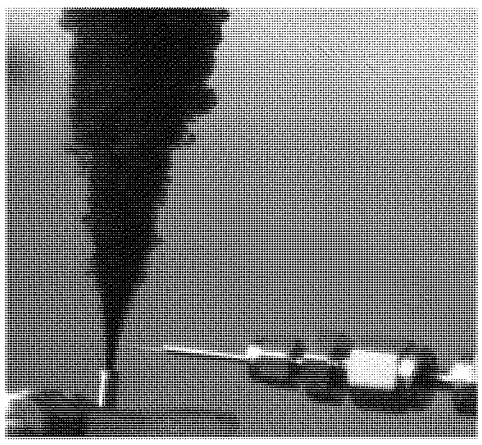
temperature as the oil enters the sea, it is unlikely that this will reduce the effectiveness of the dispersant in the case of most crude oil. Crude oil being released form a subsea well will often be at high temperature, although it will be rapidly chilled when it comes into contact with the cold water at deep releases. If a crude oil has a very high pour point due to a very high wax content, it is possible that it would become solid on entering the water and then be dispersed as a plume of solidified wax droplets.

A potential limitation to subsea dispersant use could be the effectiveness of dispersant addition. Dispersant needs to be added to the oil as the oil and gas enters the water. Studies (Brandvik et al, 2014 and 2013 and Johansen et al., 2013) have shown that the time available for the surfactants in the dispersant to influence droplet formation after the oil is released is very limited, before the dispersant is carried away in the entrained water at the release:

- If injecting dispersant into the oil and gas before the release, for example injecting dispersant into a broken riser pipe, the dispersant should be injected no more than about six release diameters, or four milliseconds flow time, before the release.
- If the dispersant is to be added to the turbulent outflow from an oil and gas release, the dispersant should be added only slightly above the oil and gas release at a maximum of 10 diameters of the release.



Photograph from a test tank showing the injection of dispersant into a release; the dispersant is visible as a white line being sucked into the rising plume of oil
Credit: SINTEF

The SSDI systems developed take into account the above requirements to allow effective operations. Injecting dispersant into the oil before it releases at the discharge point may be better than spraying into the release oil jet near the discharge point. The injection point isn't likely to be very significant as long as the dispersant is injected within the energetic jet before it begins to break into individual droplets. The distance outside the release point where this occurs will depend on the release conditions.

If the dispersant can't be injected into the oil and gas flow before it is released, than the next best option is to get as close to the release point as possible. Dispersants have been shown to be effective under test conditions as long as they are injected into the energetic solid jet of oil before it breaks into droplets. A key requirement for injecting outside the release point will be to ensure that the dispersant is distributed around the jet and not just into one side. The most effective way to do this may be using injection rings.

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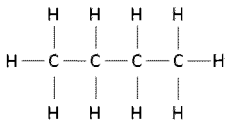
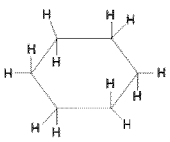
Toxicity and biodegradability of oil

Chemical compounds in crude oils

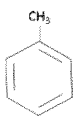

alkane

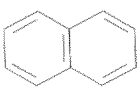

cycloalkane

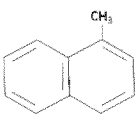
aromatic (benzene)

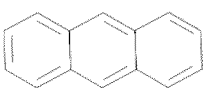
Crude oils are composed of a large number of individual chemical compounds. Almost all of these are hydrocarbons, composed of only hydrogen and carbon. Hydrocarbons can be classified by molecular weight, or carbon chain length, and the majority of hydrocarbons in crude oil contain from 5 to 35 carbon atoms. Hydrocarbons can also be classified according to chemical type; alkanes (paraffins), cycloalkanes (naphthenes) and aromatic compounds (containing one or more benzene rings). The relative proportions of these chemical compounds differ between crude oils and are responsible for the range of physical properties that crude oils exhibit. The majority of hydrocarbons in most crude oils are alkanes and cycloalkanes and they can range from volatile liquids to non-volatile liquids or solids (waxes) depending on their size (number of carbon atoms) and the prevailing temperature.

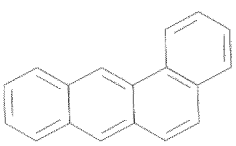
Potentially toxic chemical compounds in oil

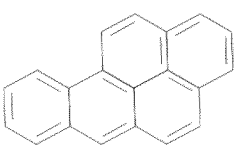

1-ring: toluene


2-ring: naphthalene


2-ring: 2-methylnaphthalene


3-ring: anthracene


4-ring: benzo(a)anthracene


5-ring: benzo(a)pyrene

Most alkanes and cycloalkanes have a limited potential to cause toxic effects to marine organisms due to their low water solubility. Aromatic hydrocarbons are partly water-soluble and are generally considered to be the toxic component of crude and fuel oils to aquatic organisms (Anderson et al., 1974; Di Toro et al., 2007).

Aromatic chemical compounds in oils

- **One-ring aromatic compounds**: These are benzene, toluene, ethylbenzene and xylenes and are often referred to as BTEX compounds and crude oils contain from about 0.5% up to 5% BTEX. Gasoline can contain up to 40% BTEX. BTEX compounds are relatively soluble in water, but they are also comprise the majority of VOCs and will rapidly evaporate into the air from floating oil.
- **Two-ring aromatic compounds**: Naphthalene and alkyl-substituted derivatives. Different crude oils contain from 0% to 0.4% of naphthalene and from 0% up to 1% or more of substituted naphthalenes. These compounds are less water-soluble than BTEX and of moderate volatility.
- **3-, 4- and 5-ring Polycyclic Aromatic Hydrocarbons (PAHs)**: Crude oils contain from 0 ppm to several hundred ppm of the 3-ring aromatic compounds, but much less, typically 1 to 10 ppm, of the individual 4-ring and 5-ring compounds. These PAH compounds are not volatile and the 3- and 4-ring compounds are slightly water-soluble.

Toxicity testing of dispersants and dispersed oil

Toxicity testing of dispersants and dispersant / oil mixtures (to produce dispersed oil) is carried out for different purposes and using a variety of toxicity test methods. The original intention of toxicity testing of dispersants was to ensure that the use of toxic industrial detergents, such as those used in massive quantities at the *Torrey Canyon* oil spill in the UK in 1967 (Smith, 1968), would not be repeated. In order to be approved, dispersants had to exhibit a toxicity less than a level deemed acceptable.

A 96-hour or 48-hour LC_{50} (Lethal Concentration to 50% of test population) toxicity test with a variety of test species was used to determine the toxicity of the dispersants. The purpose of the 48- or 96-hour

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LC_{50} toxicity test is to determine the concentration of dispersant in water that kills half the creatures exposed for the specified time. The test can therefore rank one dispersant as being more or less toxic than another dispersant. The exposure regime (concentration of dispersant in the water and exposure duration) in an LC_{50} test does not simulate the exposure to dispersant that a marine organism would experience if the dispersant was used on spilled oil at sea.

In the USA, the toxicity tests required by the US EPA for dispersants to be included on the NCP (National Oil and Hazardous Substances Pollution Contingency Plan) Product Schedule involves testing with two US EPA standard species; inland silverside fish (*Menidia beryllina*) and mysid shrimp (*Americamysis bahia*). As noted above, the exposure regime of the LC_{50} toxicity testing procedure does not simulate dispersant use on spilled oil at sea because the concentrations used in the test are much higher, and the duration of exposure is much longer, than would occur at sea. However, LC_{50} toxicity testing provides a way of assessing the relative magnitude of toxic effects that could be caused by dispersants or dispersed oil under the test's exposure conditions.

At the time of the *Deepwater Horizon* incident, eight dispersants on the NCP Product Schedule were tested for toxicity (Hemmer et al., 2010).

The measured levels of toxicity in the LC_{50} tests were ranked on a five-level scale from 'Very Highly Toxic' to 'Practically Non-toxic' as used by the US EPA for interpreting the results of LC_{50} tests (EPA Online. 2012).

EPA ecotoxicity categories (ppm = parts per million)	Mysid shrimp 48 hour LC_{50}	Silversides fish 96-hour LC_{50}
Very highly toxic: <0.1 ppm		
Highly toxic: 0.1-1 ppm		
Moderately toxic: >1-10 ppm		Dispersit SPC 1000
Slightly toxic: >10-100 ppm	Dispersit SPC 1000 Nokomis 3-AA **Corexit 9500A** Nokomis 3-F4 ZI -400	Nokomis 3-F4 Nokomis 3-AA ZI -400 Saf-Ron Gold Sea Brat #4
Practically non-toxic: >100 ppm	Saf-Ron Gold JD-2000	**Corexit 9500A** JD-2000

The majority of the dispersant used at the *Deepwater Horizon* incident was Corexit 9500A and that was ranked as 'slightly toxic' to mysid shrimp and 'practically non-toxic' to silversides fish in the LC_{50} toxicity tests.

The same toxicity testing methodology used for listing on the NCP Product Schedule was used by the US EPA (EPA ORD, 2010) to determine the relative magnitude of the toxic effects that could be caused by:

- Mechanically dispersed Louisiana Sweet Crude (LSC) oil.
- The dispersant used during the *Deepwater Horizon* response; Corexit® EC9500A, and
- LSC crude oil dispersed by using a mixture of 1:10 of Corexit® EC9500A and LSC.

The results summarized below clearly show that the dispersant alone causes less toxic effect than the crude oil alone. The dispersant alone is considered to be 'practically non-toxic' to the fish species and only 'slightly toxic' to the shrimp while the mechanically dispersed crude oil is rated as being 'moderately toxic' to both. The crude oil dispersed with the dispersant has the same rating as the mechanically dispersed crude oil of 'moderately toxic' to both species. In this case the measured toxic effects are caused by the oil, not the dispersant.

US EPA's aquatic toxicity testing summary results for the spilled oil, dispersant and dispersed oil from the *Deepwater Horizon* response (EPA ORD, 2010)

	Louisiana Sweet Crude (LSC) oil		Dispersant (Corexit® EC9500A)		Dispersed oil (LSC + Corexit® EC9500A)	
EPA ecotoxicity categories (ppm = parts per million)	Mysid shrimp	Silverside fish	Mysid shrimp	Silverside fish	Mysid shrimp	Silverside fish
Very highly toxic: <0.1 ppm						
Highly toxic: 0.1-1 ppm						
Moderately toxic: >1-10 ppm	2.7 ppm	3.5 ppm			5.4 ppm	7.6 ppm
Slightly toxic: >10-100 ppm			42.0 ppm			
Practically non-toxic: >100 ppm				130.0 ppm		

The LC_{50} toxicity testing used a 1:10 mixture of dispersant to oil and this is more dispersant than would be used in subsea dispersant use where ratios of 1:100 or 1:50 would be typical.

In actual dispersant use on spilled oil on the sea surface or by subsea dispersant injection, the exposure regime for marine organisms to dispersed oil will be a result of the circumstances of the oil release.

Exposure to oil, dispersed oil and water-soluble compounds from the oil

A fundamental basis of toxicology is that the magnitude of the effect caused to an organism by a chemical compound is dependent on the exposure of the organism to the chemical compound. Exposure is a function of exposure route, concentration of the chemical to which the organism is exposed and the duration of exposure.

If a subsea oil release has occurred, it is inevitable that some marine organisms will be exposed to elevated concentrations of dispersed oil droplets and water-soluble compounds from the oil in the water. If the subsea release is a subsea blowout of oil and gas being released at high pressure and at high velocity, all of the oil will be released into the water as a plume of oil droplets. A substantial proportion of the released oil volume may be converted to very small oil droplets by the intense turbulence produced by the oil and gas release. In these circumstances, many of the lower molecular weight aromatic compounds (the BTEX and the 2- and 3- ring PAHs) will be rapidly dissolved from the oil into the water.

These compounds have the potential to cause toxic effect to the marine organisms that are in the vicinity of the subsea blowout by the exposure route of absorption through the gills and other organs. Any marine organisms near the subsea blowout will also be exposed to very high concentrations of dispersed oil in water. The plume of dispersed oil droplets, gas bubbles and entrained water containing the water-soluble oil compounds from the oil will rapidly rise through the water column. The primary risk of the water-soluble compounds from the oil is therefore to pelagic organisms (those in the water column), rather than to benthic organisms (those that live either in or on the seabed) or the demersal organisms that live near the seabed.

The concentrations of dispersed oil and water-soluble compounds from the oil will rapidly decrease as the buoyant plume entrains water and is diluted as the plume rises through the water column. However, while the blowout continues there will always be a very high concentrations of dispersed oil and water-soluble compounds from the oil in the water as the crude oil continues to be released into the sea.

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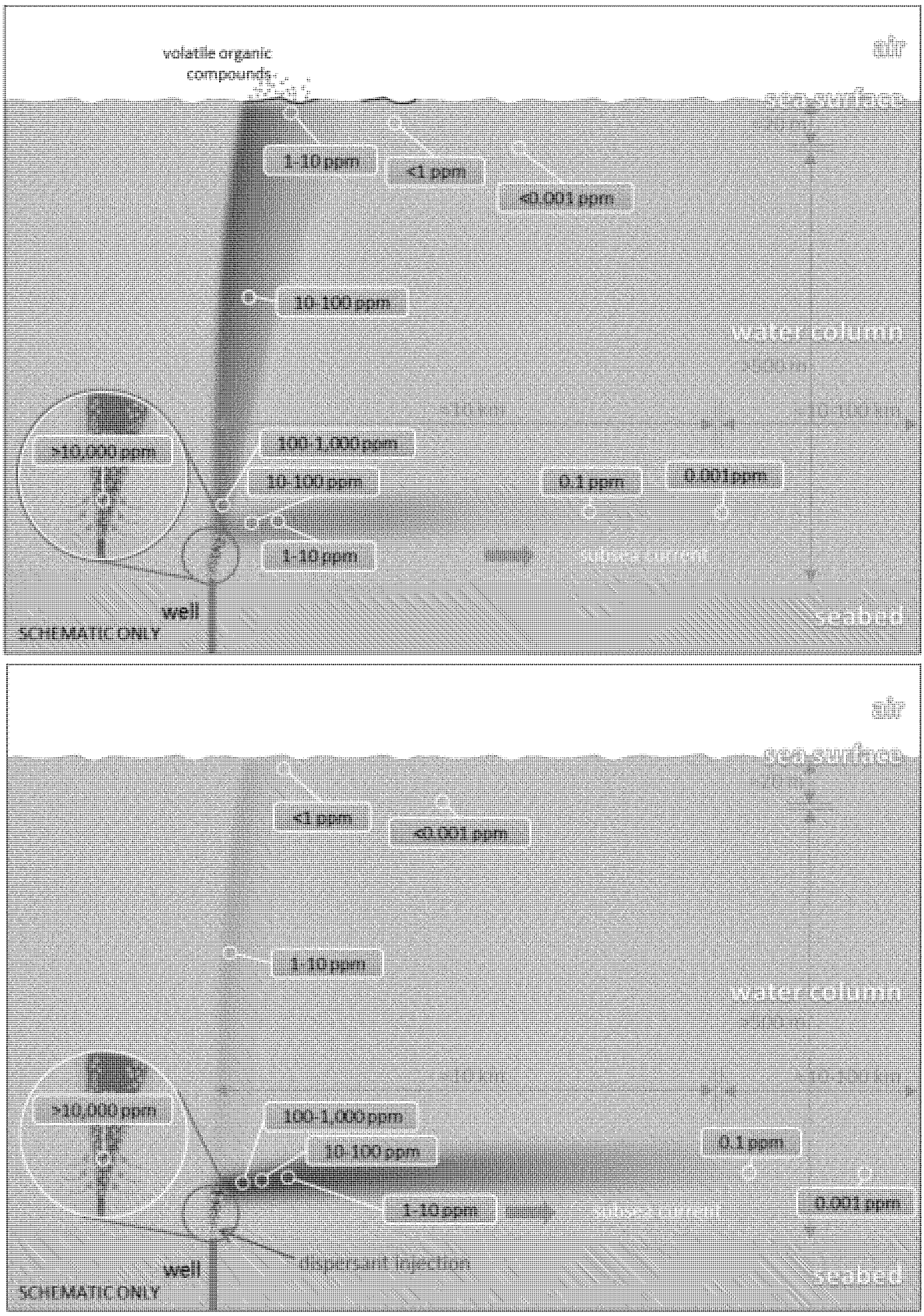

Figure X. Schematic representation of the likely oil concentrations in the vicinity of a high pressure subsea release both with (below) and without (above) dispersant addition. ppm = part per million.

Note: Dispersed oil plumes in the water column are not visible and require sensitive instrumentation to detect them, as the dispersed oil is diluted into the water column (not to scale)

Effect of subsea dispersant use

If subsea dispersant use is effective, the oil droplets entering the water as a plume will be smaller in size. This will enhance the rate of transfer of the water-soluble compounds from the oil into the water because the oil/water surface area is increased with smaller oil droplets. This will result in higher dispersed oil and water-soluble compound concentration in the water in the close vicinity of the release. Although SSDI will increase concentrations, they may already be relatively high without dispersant use. Therefore the potential for toxic effects to be caused to marine organisms present in the vicinity of the subsea oil and gas release is increased by subsea dispersant use but from an already high 'baseline' condition. Oil that is dispersed by SSDI will be present as subsea plumes of dispersed oil at low concentration. These plumes will drift with the subsea currents and the dispersed oil will be biodegraded without reaching the sea surface.

Exposure of marine organisms by ingestion of dispersed oil droplets

There is also an exposure route of marine organisms to the higher molecular weight PAHs through ingestion of food. Filter feeding organisms that prey on plankton can ingest naturally or chemically dispersed oil droplets when they are of similar size to some plankton. Relatively simple organisms, such as bivalves, cannot biochemically process the higher molecular weight PAHs in the oil and these PAHs can build up ('bio-accumulate') in some organs (Neff and Burns, 1996). These compounds will subsequently be lost by depuration (transfer of compounds from muscle tissue of fish and into the surrounding water) into clean water. Predators that consume oil-contaminated bivalves can therefore be exposed to elevated concentrations of the higher molecular PAHs by this ingestion route. Organisms that possess livers, such as fish, can metabolize PAH and some of these metabolites are harmful. Some individual fish may be affected, but it is very unlikely that the population will be significantly harmed.

Biodegradation of oil

Oil droplets in the water column are rapidly colonized by petroleum degrading microorganisms that naturally occur in ocean environments (King et al., 2014). All of the world's oceans have natural hydrocarbon seeps (Kvenvolden, 2003), and oil degrading microbes are found in all marine environments – even cold, dark environments – having evolved to degrade petroleum from these seeps. Most of the chemical components of crude oil in these droplets has only limited water solubility and the microorganisms must inhabit the interface between the oil and the water to biodegrade the oil. Oil dispersed as small droplets has a much greater oil / water interfacial area than an oil slick floating on the sea surface. As a result, more interfacial area available for microbial attachment will result in faster biodegradation. A community of microorganisms (bacteria and fungi) consumes and degrades the oil as they grow and reproduce, and then larger protozoans and nematodes consume the bacteria. The oil is thereby assimilated into the environment (American Academy of Microbiology, 2011). Dispersed oil also rapidly dilutes. By the time that an individual droplet is fully colonized by micro-organisms and biodegradation becomes significant, concentrations of dispersed oil are likely well below 1 ppm. At these low concentrations, most marine environments have sufficient oxygen, phosphorous, nitrogen, and other nutrients to allow efficient aerobic biodegradation to proceed.

Figure X shows a photomicrograph of an oil droplet with marine oil degrading bacteria attached. It can be seen that the microorganisms (i.e., a few microns in length) that degrade oil can be much smaller than the oil droplets themselves (i.e., a few tens of microns in diameter).

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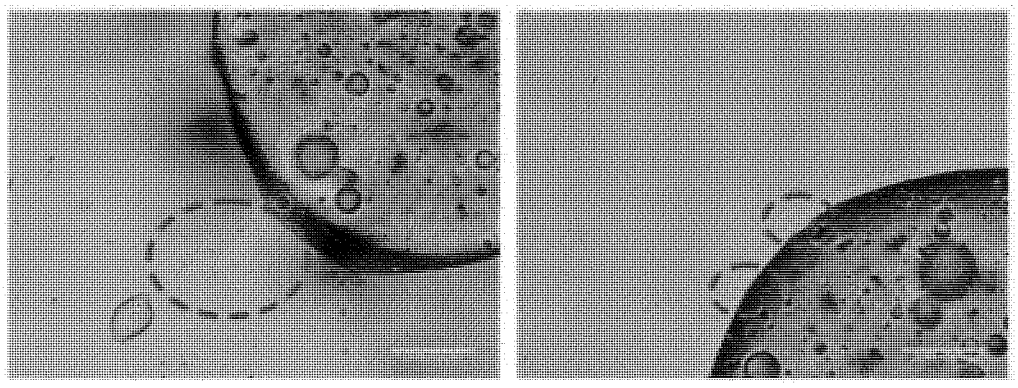


Figure X. Biodegrading microbes begin "eating" the dispersed oil droplet. The white scale bar shown at bottom right of figure is 20 microns. (Source: Hazen et al., 2010)

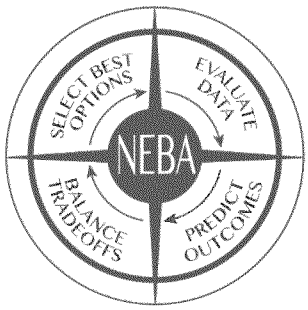
Biodegradation proceeds principally by biochemical oxidation (Atlas and Bartha, 1992; Atlas and Cerniglia, 1995; Prince, 1997; Prince et al., 2013). The different chemical compounds in crude oils will be biodegraded at different rates and to different extents (Singer and Finnerty, 1984; Lindstrom and Braddock, 2002; Campo et al, 2013). Linear chain alkanes will be most rapidly biodegraded, followed by the single-ring aromatic compounds and then by branched chain alkanes and cycloalkanes. Many complex branched, cyclic, and aromatic hydrocarbons, which otherwise would not be biodegraded individually, can be oxidized through co-metabolism in an oil mixture due to the abundance of other substrates that can be metabolized easily within the oil (Heitkamp and Cerniglia, 1987).

The ultimate fate of the majority of oil that is biodegraded is to be eventually converted into carbon dioxide and water (MacNaughton et al., 2003). There are some oil compounds that are resistant to biodegradation, often referred to as being the 'recalcitrant residue' these are largely biologically inert and are non-toxic or practically non-toxic.

The dispersed oil concentration in the water will progressively decrease to less than 1 ppm as the small oil droplets are further diluted into the water column. The surfactants and solvent in dispersants are biodegradable and therefore dispersant will also be biodegraded, usually more rapidly than the oil. The recalcitrant residue that cannot be readily biodegraded will initially be present at very low concentrations of a few ppb (parts per billion) in water as the remnants of the dispersed oil droplets. This recalcitrant oil residue will eventually be deposited over the seabed at very low concentrations over a very wide area.

To summarise, dispersing the oil either naturally or by adding dispersants allows significant enhancement of the natural biodegradation process. Effectively dispersed oil will persist in the environment for days to weeks while undispersed oil that weathers, emulsifies, and ultimately strands on shorelines could persist in the environment for multiple years.

Net Environmental Benefit Analysis (NEBA)



Net Environmental Benefit Analysis (NEBA) is a process used by the response community for making the best choices to minimize impacts of oil spills on people and the environment – see the NEBA Good Practice Guide.
NEBA works at different stages in a spill:

- NEBA is an integral part of the contingency planning process, used to ensure the response strategy for planning scenarios is well informed.
- During a response the NEBA process is used to ensure that evolving conditions are properly understood and evaluated so that the response strategy can be adapted and adjusted as necessary.
- After the immediate response effort, the NEBA process is used to ensure response end points are defined and the restoration of the environment and community assets to pre-spill use can be achieved.

NEBA involves consideration and judgment to compare the likely outcomes of using different oil spill response techniques and recommendations as to the preferred tactics based on the considerations of experienced responders and consultations with stakeholders. NEBA typically involves the following steps for identified release scenarios and should be done prior to an oil spill as an integral part contingency planning:

NEBA Step	Description
Evaluate data	The first stage is to consider where the spilled oil is and where it will drift under the influence of currents and wind - various oil spill trajectory models exist to support this. It is also useful to know how an oil will 'weather' as it drifts. This is part of evaluating the available data.
Predict outcomes	The next stage is to assess what is likely to be affected by the spilled oil if no response is undertaken. This may include ecological resources offshore, near-shore and on shorelines, alongside socio-economic resources. The efficiency and feasibility of the response toolkit should be reviewed. This covers the response techniques, the practicalities of their utilization and how much oil they can recover or treat. If areas under threat include oil-sensitive coastal habitats, the role of oil spill response at sea is to either prevent or limit the spilled oil from reaching these habitats. Previous experience can help assess which oil spill response techniques are likely to be effective. Pragmatic, operational considerations should form a very important part of the NEBA process applied to all feasible response techniques.
Balance trade-offs	The advantages and disadvantages of the potential response options are considered and weighed against the ecological and socio-economic impacts of each to understand and balance the trade-offs.
Select best options	The process concludes with the adoption of response technique(s) within contingency plans that minimize potential spills' impacts on the environment and promote the most rapid recovery and restoration of the affected area.

Step 1 Evaluate data

A very important aspect of oil spill contingency planning is using realistic oil release scenarios (see Contingency Planning GPG). Various subsea oil release scenarios, up to and including a Worst Credible

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Case Discharge (WCCD), should be developed. The predicted prevailing conditions must be taken into account.

Modelling should then be conducted to assess how the released oil will behave. Several computer models are available for modelling subsea oil and gas blowouts. The model needs to take into account the relevant factors such as the well's and metocean characteristics including currents, temperatures etc., throughout the relevant depths.

Work is still underway to develop models that accurately predict the oil droplet size distributions produced under a wide range of release conditions.

Step 2 Predict outcomes

Combining sensitivity mapping (see Sensitivity Mapping GPG), with modelling can indicate which ecological resources and socio-economic resources (offshore, near-shore and on shorelines) are likely to be affected by the oil if no response is undertaken. The ways in which oil can impact various ecological and socio-economic resources and the factors that can influence these impacts are described in the following GPGs:

- Impacts of oil spills on marine ecology (IPIECA-OGP, 2015a)
- Impacts of oil spills on shorelines (IPIECA-OGP, 2015b)

Feasibility of using a response technique

The likely effectiveness and feasibility of conducting the different response techniques under the range of likely prevailing conditions should be reviewed. This covers the response techniques, the practicalities of their utilization and how much oil they can recover or treat in the time that is likely to be available for their use. Pragmatic, operational considerations should form a very important part of the NEBA process applied to all feasible response techniques.

In considering a response to a subsea oil release, the decision must be made as to whether the response should be conducted subsea (with subsea capping, containment and recovery or subsea dispersant use) or to wait until the released oil has risen to the sea surface where the response could be by mechanical containment and recovery, controlled burning or dispersant use. The particular characteristics of the subsea oil release scenario and released oil and gas behaviour will inform this decision.

- At a subsea oil and gas blowout in deep water, where the gas will be dissolved in the water and not reach the sea surface, the use of surface vessels to deploy subsea capping stacks, subsea containment & recovery systems and subsea dispersant injection equipment may be a feasible response.
- However, at a subsea oil and gas blowout (with similar hydrocarbon flows and pressures) in more shallow water, where the gas will not be totally dissolved in the water and will reach the sea surface, the use of surface vessels to deploy subsea equipment may not be possible because of the fire and explosion risk.

The time taken to deploy any response equipment may also be a key factor in assessing the feasibility of conducting the response. Any oil spill response is often a race against time. Once a subsea oil release has occurred, the potential for damage to be caused by the oil will be determined by the proximity of resources that could be damaged and by the prevailing conditions, such a wind direction and speed.

Mechanical recovery will always be the most important oil spill response option used. It has been in the past and will continue to be in the future because the vast majority of oil spills are small and locate d

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near stockpiles of equipment. As spills grow in size and move further away from stockpiles of equipment, mechanical recovery (because of the challenge of containing significant amounts of oil in booms) will become highly inefficient. This is the reason we need dispersants that can be applied rapidly by air or dispersants applied subsea. Dispersants can treat remote oil spills quickly because they can be deployed solely by fast-moving aircraft and not slow-moving boats. Aircraft deployment means that dispersants can treat large areas much more rapidly than boat-based response. Subsea dispersants treat the oil at a known location even more efficiently.

Step 3 Balance trade-offs

The benefits and potential risks of dispersant use can be summarized as (Lewis and Aurand, 1997):

- The benefit of dispersant use is to minimize ecological and socio-economic damage by preventing the oil from reaching sensitive coastal and shoreline habitats, where it could cause severe and long-lasting damage, and to enhance the natural biodegradation processes.
- The potential disadvantage of dispersant use is that marine organisms inhabiting the water column will be exposed to dispersed oil droplets and water-soluble oil compounds in the water column, compared to the situation if dispersants were not used. This exposure to dispersed oil has the potential to cause toxic effects to the marine organisms.

A decision to use or not use dispersants is not a black and white decision to either protect the water-column organisms or protect marine mammals, birds and turtles. Oil slicks moving across the water surface will impact any fish eggs and larvae under the slick. Further, near shore and shoreline oil will impact the juvenile life stages of many fish. Allowing slicks to drift across the water surface and strand on shorelines may impact fisheries - possibly more so than dispersing the oil if the spill occurs during critical spawning periods or the oil moves into critical nearshore habitat for juvenile fish

The trade-offs, or balance, of potential benefits and risks of sub-sea dispersant use at a subsea blowout are similar, but not precisely the same, as those of dispersant use on spilled floating oil because the circumstances are different. The potential risks posed to marine organisms by dispersed oil are different in terms of scale, location and possible consequence.

The risk of toxic effects being caused to marine organisms is related to their exposure to dispersed oil and the partially water-soluble components released from the oil Exposure is a function of concentration and duration.

1. **Exposure to dispersed oil caused by dispersant use on floating oil**
   Breaking waves passing through a localized area of an oil slick will cause the oil to be broken up into oil droplets with a range of sizes. The larger oil droplets will rapidly resurface, but the smaller oil droplets will be dispersed into the water column. The proportion of oil dispersed by natural dispersion is often low and decreases as the oil 'weathers'.

   Dispersant use greatly increases the proportion of the oil that is converted into small droplets by the prevailing wave action. Localized plumes of dispersed oil droplets are produced as breaking waves pass through the dispersant-treated slick. The concentration of oil (as droplets) in the upper water column rapidly rises to a peak of between approximately 50 and 100 ppm at these scattered locations, but then rapidly decreases the oil is diluted into the surrounding water. As the oil slick drifts under the influence of the wind, further breaking waves will cause localized clouds of dispersed oil to be produced in the water column at locations at some distance from where the previous clouds were produced and subsequently

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diluted. The peak dispersed oil in water concentrations are low and of short duration, occurring at scattered locations over a period of time under the dispersant-treated oil.

Marine organisms inhabiting the upper layer of the water column (to a maximum depth of around 5-10 m) will be briefly exposed to increased concentrations of dispersed oil droplets and water-soluble oil compounds in the water column, compared to the situation if dispersants were not used. Some exposure will occur if dispersants are not used, due to natural dispersion; see surface dispersant GPG.

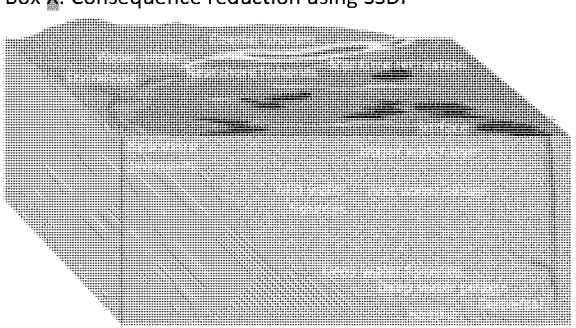
2. **Exposure to dispersed oil caused by SSDI at a sub-sea oil release**

The continuous release of large amounts of oil and gas from a point source will produce high concentrations of dispersed oil, and of the water-soluble components from the oil, in the water close to the release. The dispersed oil concentration in the water will be diluted and decrease as the plume rises and drifts away. The use of SSDI will cause a further increase in these already high dispersed oil in water concentrations close to the release. These high dispersed oil in water concentrations close to the source will be maintained for as long as the oil and gas release continues (as illustrated in Figure X).

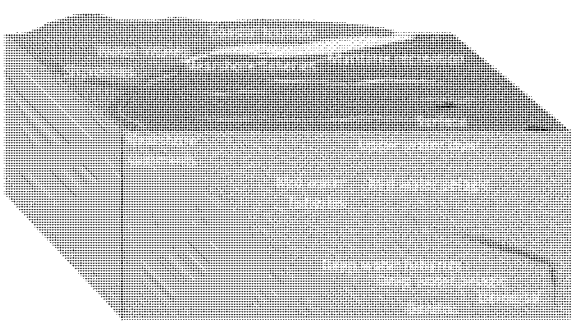
The exposure regime to dispersed oil and water-soluble oil compounds in the water column experienced by marine organisms will be dependent on their proximity to the release and the direction of plumes' drift. Organisms close to the release will be exposed to high concentrations of dispersed oil for prolonged periods, even when SSDI is not used.

Dispersant use on floating oil will cause localized elevations in dispersed oil concentrations in the water from very low levels to moderate levels, but only for a short duration. Subsea dispersant use at a subsea blowout will cause the dispersed oil concentration in the water closer the release to be increased and this exposure will continue as long as the blowout and subsea dispersant use continues. The actual effects of the dispersed oil exposure regime produced by SSDI will depend on the marine organisms that are present in the vicinity of the subsea oil and gas release or near the drifting subsea plumes of dispersed oil at very low concentration. In general, the population density in deep water is less than that present nearer to the sea surface.

Box X: Consequence reduction using SSDI



No response scenario



Scenario with effective SSDI

This representative scenario indicates of how successful SSDI can reduce the overall consequences of a release and thereby achieve net environmental benefit.

Note this example is illustrative and that individual contingency planning cases need to take into account the specifics of an operation, including the local environmental resources, their ecological, commercial and cultural value and their seasonality.

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Environmental compartment		Representative population / resources	Potential relative consequence* with no response	Potential relative consequence with SSDI
Seabed benthic zone		Burrowing organisms	Insignificant	Insignificant
Water column	Near seabed demersal zone	Flatfish	Insignificant	Insignificant
	Deep water pelagic (>400 m)	Round body fish	Small	Moderate
	Mid water pelagic (<400 m)	Round body fish	Small	Small
	Upper water layer (<20 m)	Plankton	Moderate	Insignificant
	Nearshore water (<10 m)	Coral reef	Moderate	Insignificant
Sea surface		Seabirds/sea mammals	Very large	Small
Shoreline	Nearshore sediments	Seagrass	Moderate	Insignificant
	Wetlands	Burrowing organisms	Very large	Insignificant
	Rocky shores		Moderate	Insignificant
	Sandy shores		Moderate	Insignificant
Socio-economic resources	Coastal tourism		Very large	Small
	Inshore fisheries and aquaculture**		Large	Small
	Mid water fisheries**		Small	Moderate
	Deep water fisheries**		Insignificant	Large
	Seawater intakes		Very large	Small
	Maritime recreation		Very large	Small

* Relative consequence categories take into the account a variety of factors, including the sensitivity of habitats, species or populations, the geographic extent of an area that may be affected, the anticipated recovery time and socio-economic value of a resource, if applicable.

** Fisheries authorities are likely to impose a precautionary fishing ban or exclusion to protect perceived risks to human health and market confidence. A ban typically remains until there is evidence that fish are safe for consumption. Such bans can increase the consequence to fisheries through enforced loss of earnings, rather than through impacts on fish populations or stocks.

The essential element of NEBA considering subsea dispersant use, and comparing it with the probable effectiveness of other response techniques, will be to compare the probable outcomes of:

- No response, i.e. not using subsea dispersant use or other response, with
- Those of using subsea dispersant use.

Any 'trade-off' consideration of subsea dispersant use has to consider the amount of severe and long-lasting damage to oil-sensitive coastal habitats and socio-economic resources that can likely be prevented by dispersant use and compare that with the localized effects that might be caused to the marine environment by dispersant use. Box X provides an example scenario illustrating how the use of SSDI can achieve a net benefit compared to no response.

Step 4 Select best options

In Step 4 of NEBA, data, viewpoints and trade-offs are taken into account in order to select the optimum response strategy for the planning scenario or the prevailing incident conditions. This stage of NEBA relies on planners and stakeholders reaching consensus on the priorities for protection and the acceptable balance of trade-offs.

The key objective of planning for and executing a response is to implement those techniques that at any moment in time have the greatest net benefit. For example, in an offshore marine incident, treating or recovering as much oil as close to the source as possible, will have the greatest benefit, before it has

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had a chance to weather and spread out making other response options less effective and increasing the chances of more oil reaching sensitive areas, international boundaries or the shoreline.

Examples release scenarios and the NEBA associated with their response planning are given in Annex 1.

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Regulations regarding dispersant use

A report, "Regulatory approval of dispersant products and authorization for their use" has been produced by the IPIECA-OGP Oil Spill Response Joint Industry Project (JIP) (IPIECA 2014) to provide an overview of the principles of regulations concerning dispersants.

Dispersant regulations have been divided into the following two categories:

1. **Dispersant product approval** regulation that describes which dispersants would be approved for use in national waters.
2. **Dispersant use authorization** regulation that defines where and when approved dispersant products may be authorized for use on spilled oil in national waters.

Dispersant product approval regulations for subsea use

The same considerations for dispersant product approval apply to dispersants used subsea and on floating oil, namely that:

- A dispersant should meet or exceed a threshold for effectiveness (or 'efficacy').
- A dispersant should not exceed a maximum toxicity threshold to marine life. Care needs to be taken when considering dispersant toxicity versus the toxicity of the dispersed oil (dispersant plus oil). When approving a dispersant for use, the maximum toxicity threshold of a candidate dispersant is usually set at either:
    - a level where the oil and dispersant mixture is no more toxic than the oil alone at the same exposure levels; or
    - if the dispersant is tested alone, at a level which is significantly less toxic than a reference toxicant.

  Note: concerns over the toxicity of dispersed oil should be considered during dispersant use authorization (i.e. when and where dispersant use may be allowed).
- A dispersant should be readily biodegradable and not contain persistent harmful constituents. This may require additional information to be provided as part of the product approval process.

Subsea dispersant use at the *Deepwater Horizon* incident employed the same dispersants that have been widely used around the world on floating oil.

Dispersant use authorization regulations for subsea use

To date, the USA is the only country that has had experience with regulating subsea dispersant injection as a response technique. Following the *Deepwater Horizon* accident, the National Response Team published guidance on Environmental Monitoring for Atypical Dispersant Operations (NRT, 2013), and began the process of revising the National Contingency Plan. The American Petroleum Institute (API, 2013) has developed a similar monitoring guidance document that is focused more toward collecting information needed to make operational decisions regarding continued use of SSDI.

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Part Two: Experience

The Deepwater Horizon accident

Subsea dispersant injection (SSDI) was used for the first time to treat the uncontrolled release from the Macondo well associated with the *Deepwater Horizon* incident in 2010. In order to understand the rationale for SSDI to be used it is necessary to consider the circumstances of the incident.

On the evening of 20 April 2010, a gas release and subsequent explosion and sinking occurred on the *Deepwater Horizon* oil rig working on the Macondo exploration well in the Gulf of Mexico, approximately 42 miles (68 km) south-east of Venice, Louisiana. As the drilling unit sank, the marine riser with the drill pipe inside connecting the unit to the blowout preventer and well below separated from the sinking *Deepwater Horizon* and collapsed to the seafloor. Oil and gas continued to flow from the broken and buckled riser (a pipe previously connecting the wellhead on the seabed to the rig on the sea surface) after the *Deepwater Horizon* rig had sunk.

The accident involved a well integrity failure, followed by a loss of hydrostatic control of the well. The blowout preventer (BOP) failed to seal the well after the initial explosions. A major effort was undertaken to seal off and stop the continuing oil and gas flow. Within weeks, work had begun on the drilling of two relief wells.

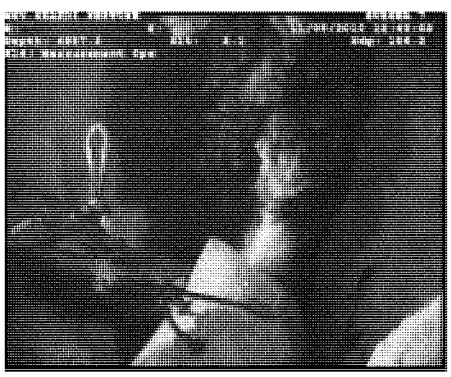
Within days of the accident occurring, the USA's federal government established a Unified Area Command to manage the response effort to the oil release. The biggest oil spill response operation in history was initiated. A wide variety of oil spill response techniques were used to try to prevent oil from reaching the shore, contaminating sensitive ecological resources and disrupting the local economy, particularly tourism and fisheries:

- Large-scale offshore skimmers and shallow water equipment to skim the floating oil.
- Where weather, sea conditions, distance from shore and other conditions made it safe and appropriate, the Unified Command also conducted controlled in situ burning of oil.
- Dispersants were used in various ways.
- Physical shoreline protection, including the deployment of 3.8 million feet (1,160 km) of hard boom and 9.7 million feet (2,960 km) of absorbent soft boom.

The well was capped on 10 July and the oil and gas release was stopped on 15 July. Oil and gas had flowed into the waters of the Gulf of Mexico for 87 days. In January 2015, the USA District Court concluded there is no way to know with precision how much oil was discharged into the Gulf of Mexico but estimated a total of 3.19 million barrels (507,000 m^3).

Subsea oil and gas release at *Deepwater Horizon*

There are several characteristics of the subsea oil and gas release that occurred at the *Deepwater Horizon* that determined the fate of the oil. Some parameters are not known with accuracy and some became the subject of much speculation and legal contest; such proceedings continue at the date of the preparation of this guide. Other facts are not disputed and are known with certainty.



Oil and gas being released from the broken riser on May 11th 2010 (credit?)

After the *Deepwater Horizon* sank, the release of oil and gas was occurring at a water depth of approximately 5,100 feet (1,550 metres), where the pressure is 150 atmospheres. This precluded direct human intervention by divers trying to assess the oil and gas release rates and shut off the flows. All subsea operations were conducted using remotely operated underwater vehicles (ROVs). Video cameras on the

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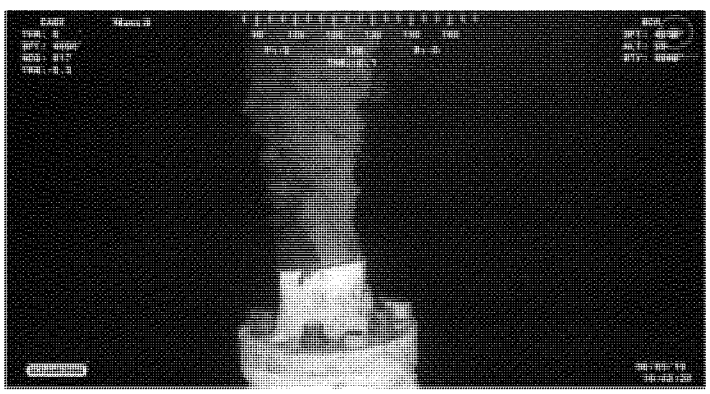
ROVs deployed to the seabed soon revealed that the oil and gas flow was continuing from two or three places along the broken and buckled riser.

Oil continued to arrive on the sea surface and a variety of techniques were tried to regain control of the source of the oil and gas and to stop the flow or to contain and recover the oil.

- A coffer dam was deployed on 7 May, but solid methane hydrate formed altering the buoyancy of the coffer dam preventing it from being properly placed to collect oil.
- A pipe, known as the RITT (Riser Insertion Tube Tool), was inserted into the broken riser on 14 May to collect some of the outflow and recover it to a vessel on the sea surface. The RITT collected an average of 2,000 barrels (320 m^3) per day of oil until it was removed to allow the "Top Kill' procedures to proceed.
- The "Top Kill" operation was unsuccessful on 29 May and preparations were made to proceed with the Lower Marine Riser Package (LMRP) Containment System Plan.
- The riser was cut off on 3 June and the LMRP/'Top Hat' containment system was put in place in place. This recovered oil and gas siphoned through riser to vessel Discoverer Enterprise at a rate of approximately 15,000 bbls (2,400 m^3) per day.
- A second containment system (subsea manifold) was attached to the BOP on 16 June and the recovered oil and gas was flared via the Q4000 platform at a rate of approximately 8,500 barrels (1,400 m^3) per day.
- The well was capped on 10 July and the oil and gas release was stopped on 15 July.



Hydrocarbons (oil and natural gas) escaping from the end of the riser tube after it was severed on June 3rd immediately above the Macondo well BOP stack. (Modified from BP video from ROVs.)

The amounts of oil and gas being released into the deep sea at the *Deepwater Horizon* incident are not known with accuracy and could not be measured directly at the time. Many estimates of the rate of oil and gas flow were made, both during and after the incident, but the precise amounts remain unknown. It was obvious that some of the oil that was being released was reaching the sea surface because the oil slick continued to be formed in close proximity to the release location, even though the oil on the sea surface was drifting away under the effects of the prevailing wind and currents. The area of the floating oil slicks increased with time. However, it is very likely that a proportion of the oil released at the source did not subsequently arrive on the sea surface and was being dispersed by the inherent mixing energy of the release.

The oil was not being released as a continuous stream of liquid. Instead, due to the turbulence created in the water by the release conditions, the oil and gas were being released into the water as a plume of small oil droplets and gas bubbles. The size distribution of the oil droplets and gas bubbles produced would have been a function of several parameters including:

- The flow rates of gas, oil and the Gas to Oil Ratio (GOR);
- The pressures and temperatures of the released fluids (the Macondo well was into a High-Pressure High-Temperature oil and gas reservoir);
- The size and configuration of the orifice through which the oil and gas was being released, and
- The pressure and temperature of the water into which the oil and gas was being released.

As noted above, some of these parameters are known with certainty and precision, but others can only be estimated with much less certainty or accuracy. Studies and modelling conducted after the *Deepwater Horizon* incident (for example Socolofsky et al., 2011), plus measurements made at the time

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of the incident and in the months afterward (OSAT 1, 2010), confirmed the general characteristics of the oil behaviour previously shown in Figure X.

Dispersant use at the *Deepwater Horizon* accident

Dispersant use on oil on the sea surface

Oil spill response commenced on 22 April, when aircraft first sprayed dispersant on to floating oil. This was done under the direction of the Federal On-Scene Coordinator (FOSC) and dispersant use had been pre-authorized in the RRT's (Regional Response Team) oil spill contingency plan. Aircraft sprayed dispersant onto oil outside a 5 nautical mile radius safety exclusion zone imposed around the vessels dealing with the source control efforts. Dispersant spraying was conducted closer to the source from ships and boats. The objective was to disperse the floating oil into the water column and also to suppress the build-up on Volatile Organic Compounds (VOCs) in the air so that response personnel would not be exposed to them.

As the oil spill response operation grew, more aircraft were used for spraying dispersant onto the floating oil. The amount of dispersant sprayed from aircraft one week into the response was 138,024 gallons (522.5 m^3) and was rising rapidly. It became apparent to many people that the oil spill response effort could become a prolonged operation. The very large quantity of dispersant that was being used, greater than at any previous oil spill response, and the probability that dispersant spraying could continue for an indefinite period of time, concerned the Environmental Protection Agency. It also became apparent that allowing the oil to rise to the sea surface as a very large and scattered oil slick and then spraying dispersant onto it was not the most effective way of using dispersant.

Consideration of subsea dispersant use

More effective ways of using dispersant were sought. Adding dispersant subsea, directly to the oil as it was released, was considered. Subsea dispersant addition could have several possible advantages:

- It would enhance the safety of the oil spill response and source control efforts by reducing the amount of oil on the sea surface. This would reduce the potential exposure of response personnel on the surface vessels to Volatile Organic Compounds (VOCs) evaporating from the oil.
- It would reduce the need for subsequent mechanical recovery, burning, surface dispersant use and shoreline protection / treatment by reducing the amount of floating oil.
- It would have a higher encounter rate compared to spraying dispersant onto floating oil. The dispersant would be effective at lower treatment rates and this could reduce the total amount of dispersant needed for the response.
- It would be able to proceed continuously day and night (24/7) while dispersant could only be sprayed from aircraft during daylight hours.
- It would not be affected by inclement weather and sea conditions that would prevent or limit other at-sea response techniques.

However, there were also many uncertainties and questions about subsea dispersant addition, including:

- Subsea dispersant addition had never been done before. Would it work? And if it did, what would be the consequences?
- What would be the long terms effects of subsea dispersant use?
    - Generating a prolonged point-source of large amounts of dispersed oil.
    - How to conduct a Net Environmental Benefit analysis (NEBA) if the subsea environment is not extensively studied?

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- Would biodegradation of the dispersed oil occur in the low temperature water at significant depth?
- If it did, would oxygen be depleted to very low levels?

Testing subsea dispersant use

Because of the magnitude of the oil release, the RRT authorized BP to conduct tests of this new subsea dispersant addition approach. A series of tests with limited amounts of dispersant were conducted on 30 April, 2-4 May, 10-11 May.

A series of aerial photographs taken during the tests with subsea dispersant injection conducted from 9-12 May are presented and discussed in Box X. It is not possible to accurately quantify the total amount of oil on the sea surface from such photographs (or by any currently-existing remote sensing methods) and the photographs show only a small proportion of the total a rea of the oil on the sea surface. A quantitative assessment of how effective subsea dispersant use was is therefore not possible. However, the photographs supply good qualitative evidence of the effect of subsea dispersant use. The photographer was able to confirm that observed reduction in surface expression of oil extended beyond the area covered by the images.

Although this was not quantitative evidence of the effectiveness of subsea dispersant injection, it was sufficient to for subsea dispersant injection to be allowed proceed with suitable monitoring.

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Box X: Visual evidence of the effectiveness of SSDI (images copyright Ocean Imaging)

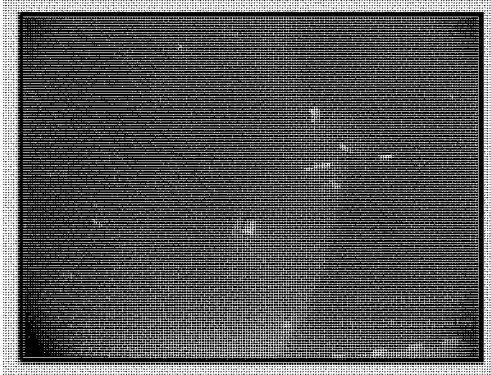


Photo 1

9 May, 08:52

Surface expression of oil prior to dispersant injection, visible as floating oil above the release source as a continuous layer. Oil being released from the broken riser is constantly rising up through the water column and arriving on the sea's surface.

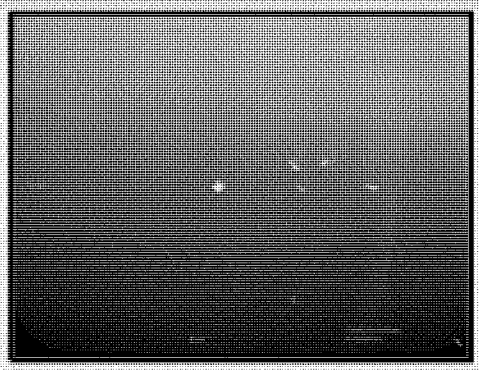


Photo 2

10 May, 08:40

Photo 2 show the same aerial view three hours after dispersant started to be injected into the oil and gas flowing out of the end of the broken riser through a pipe guided in by the ROV.

The area of floating oil in Photo 2 is obviously a lot less than that in Photo 1. A reasonable interpretation is that the most of the oil was no longer arriving at the sea surface.

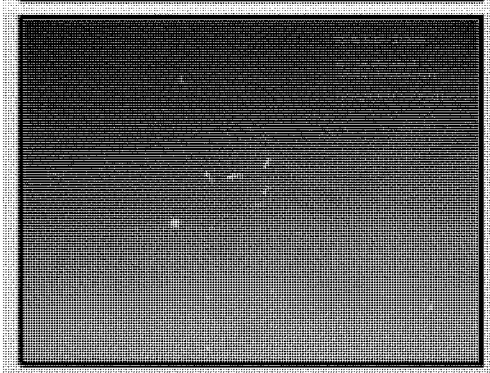


Photo 3

10 May, 17:05

Photo 3 shows the floating oil after eleven hours of dispersant being injected subsea. Only scattered remnants of oil are visible on the sea surface.

Subsea dispersant injection was then stopped.

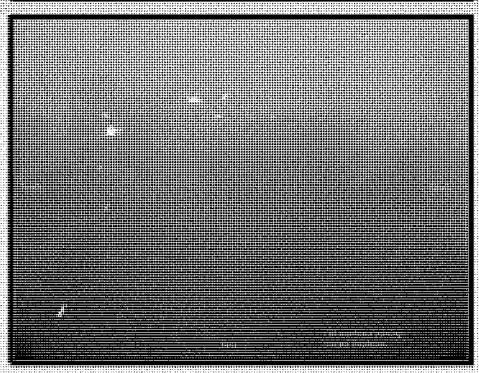


Photo 4

11 May, 09:10

Photo 4, taken five hours after the subsea dispersant injection was stopped, shows that the extent of floating oil had significantly increased. This indicated that oil that had previously been dispersed subsea by the dispersant injection was now reaching the sea surface.

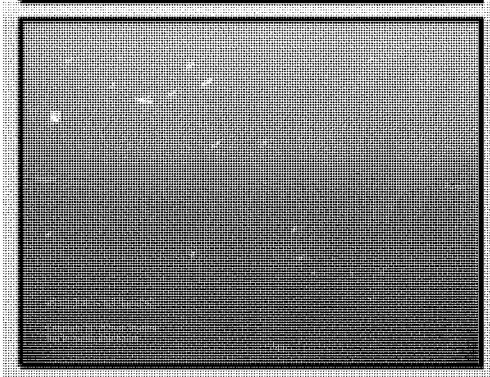


Photo 5

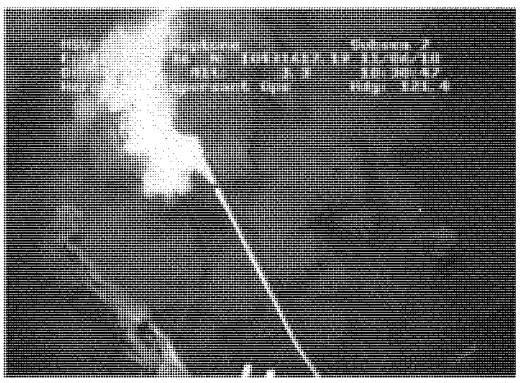
12 May, 08:35

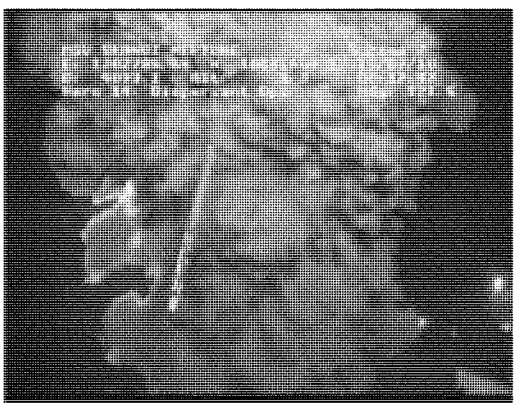
Photo 5, taken 28 hours after dispersant injection had ceased, shows that the extent of floating oil is similar to that before subsea injection was tested, although the oil is now drifting to the north due to changes in the wind.

Subsea dispersant application

Subsea method

Dispersant continued to be injected into the oil and gas flowing out of the end of the broken riser through a pipe guided in by the ROV until 3 June when the broken riser was removed. Dispersant was then added to the oil and gas flowing from the well-head and then the LMRP until the oil flow was stopped on 15 July.





The dispersant was added by a 'lance' or 'wand' held by a ROV and guided by the ROV operator. The live video feeds showed that the lance was being moved around into the release of oil and gas, plus the water that was being entrained in the plume, a few feet (around 1 m) above the well-head or LMRP. Dispersant addition using lances, or wands, of various configurations was tried (Figure X).

Subsea dispersant treatment rate

Since the oil and gas flow rates were not known and could not be measured, it was not possible to specify a dispersant treatment rate, in terms of the Dispersant to Oil Ratio (DOR) that needed to be achieved. In the absence of accurate information about the oil and gas flow rates, the dispersant was initially added at a rate of 12 gal/min (45.4 l/min, equivalent to 410 barrels of dispersant/day, but this was later reduced to 7 gal/min (26.5 l/min, equivalent to 240 barrels of dispersant/day).

The intention was that subsea dispersant addition would reduce the total amount of dispersant that would be required in the response because the addition of dispersant directly into the oil would be more effective than surface spraying on to scattered floating oil. However, some oil continued to reach the sea surface and dispersant spraying from aircraft also continued.

On 26 May, EPA and the Coast Guard issued a directive (EPA, 2010a) requiring an overall goal of reducing the total volume of dispersant used (on oil on sea surface and subsea) by 75% and to cease use of dispersant on floating oil in the absence of prior written authorization from the Coast Guard. EPA continued to allow subsea dispersant use, but only at a maximum of 15,000 gal/day, equivalent to 10.4 gal/min (39.3 l/min, equivalent to 357 barrels of dispersant/day).

Amount of dispersant used

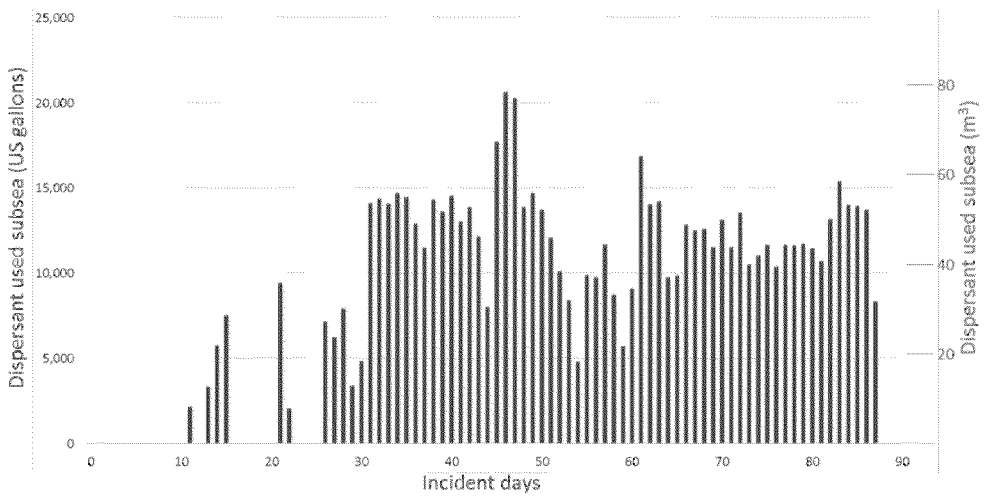
A total of just over 1.8 million gallons (nearly 7,000 m^3) of dispersant was used at the Deepwater Horizon incident.

Dispersant used at Deepwater Horizon	US gallons	m^3
Sprayed from aircraft	976,249	3,696
Sprayed from ships	93,751	355
Sub-sea	771,272	2,920
TOTALS	**1,841,272**	**6,970**

Over 40% (771,272 gallons or 2,920 m^3) of the total amount of dispersant was injected subsea.

After the test applications conducted at the end of April and during early May, the daily amount of subsea dispersant used rose to 15,000 gal/day (57 m^3/day) with an average dispersant pump rate of 10 gal/min (39 l/min) (Figure X).

After the EPA's Directive of 26 May, the average rate of dispersant addition decreased, although during 3-5 June at the time the riser was removed and the LRMP was fitted, the dispersant application rate briefly increased to 20,000 gal/day (76 m^3/day), equivalent to 14 gal/min. The daily dispersant subsea usage then continued at a rate of between approximately 8,000 to 13,000 gal/day (30 to 49 m^3/day), equivalent to 6 to 9 gal/min (21 to 30 l/min) until the oil flow stopped on 15 July.



Water column monitoring requirements

Subsea dispersant use had never been attempted before the *Deepwater Horizon* incident. The scale of the oil release and the use of dispersants in such large quantities as a response was without precedent. Monitoring of the water column was required to address the questions and concerns about subsea dispersant use, namely:

- Would the subsea addition of dispersant to the oil and gas release work?
- If subsea dispersant addition did work, what would be the consequences?
    - Where would the plumes of dispersed oil be transported to by the prevailing currents?
    - What would be the concentrations of dispersed oil in these the plumes?
    - Could these concentrations of dispersed oil cause harm to the marine organisms exposed to them?
    - Would biodegradation of the dispersed oil occur in the cold, deep water? If biodegradation did occur, would the oxygen in the water be depleted to very low levels and cause harm to marine organisms?

The EPA required monitoring of subsea dispersant to indicate the overall effectiveness of the dispersant added. They also wished to have indications of the transport of dispersed oil in the water column.

On 10 May the EPA had issued a Directive (EPA, 2010b) that BP must implement a three-part monitoring plan required for subsea dispersant use to proceed. Part 1 monitoring was required to indicate if subsea dispersant use was being successful, i.e. dispersing the oil subsea, and employed:

- Towed Fluorimeter (Turner Designs C3 fluorimeter) used at 1 m water depth to measure oil in water concentrations.
- LISST (Sequoia Scientific, Inc.) Particle Size Analysis at various intervals from surface to 550 m water depth to measure oil droplet size distributions.
- Dissolved Oxygen at various intervals from surface to 550 m water depth to detect any oxygen depletion due to biodegradation of oil.
- CTD – Conductivity, Temperature, and Depth at various intervals from surface to 550 m water depth.
- Water sampling from surface to 550 m for PAH (Polycyclic Aromatic Hydrocarbon) analysis
- Aerial Visual Observation (weather permitting)

Part 2 monitoring was required when the Part 1 monitoring indicated that subsea dispersant use was being effective. This extended the required monitoring of Part 1 to be undertaken to the sea floor at 1500 m water depth. In addition, some extra monitoring requirements were added:

- Cast (i.e. lowered, not towed) Fluorimeter – surface to sea floor
- Rototox™ toxicity testing
- UV-Fluorescence testing to detect higher molecular weight (> 3-ring) PAH fractions

Part 3 outlined the operational procedures for subsurface injection of the dispersant and included parameters such as the types of dispersant to be used, the rate of dispersant injection, how the pumping rate will be monitored and procedures for FOSC to start and stop injection

The addition of the requirement to conduct Rototox™ toxicity testing was to give an indication of any toxic effects that may have been caused by dispersed oil in the water column. Two thresholds were specified:

1. If there is a significant reduction in DO (Dissolved Oxygen) from background to below 2 mg/ l; or
2. If the toxicity tests revealed excessive exertion of a toxic response.

In the event that the thresholds were reached, and taking into account all the relevant factors including shoreline, surface water, and other human health and ecological impacts, the RRT would have determined whether subsea dispersant application should be shut down.

The monitoring requirements were subsequently modified to include monitoring of unaffected waters to provide background data and a combined CTD and water sampling rosette package.

Results of monitoring

The water column monitoring and sampling undertaken was designed to reveal:

- Measurable indications the effectiveness of subsea dispersant addition, such as the location and concentrations of dispersed oil in the subsea plumes, but also:
- The absence of negative potential consequences of subsea dispersant use such as toxic response in test organisms, or a large decrease in the dissolved oxygen content of the water.

The results of the monitoring and water sampling carried out were summarized in a report prepared by the Unified Command in a Summary Report for Sub-Sea and Sub-Surface Oil and Dispersant Detection: Sampling and Monitoring, often referred to as OSAT1 (OSAT, 2010). This report presents results on 10,000+ samples from 25 research vessels on over more than 125 cruises and 850 ship days at sea.

The data in Figure X are taken from the JAG data report 2 (JAG, 2010a) and are examples of the measurements made during monitoring of the water column at different times, dates and locations. These Figures show:

- Fluorimeter response, Fluorescence (ppb QSDE, Quinine Sulphate Dehydrate Equivalence) in black
- Dissolved oxygen content of the water (mL/L) in red
- Water density anomaly (kg/m^3) in blue

The figures are of raw data and are used only to illustrate the results obtained during the monitoring .

Fluorimetry measurements and water chemical analysis

Dispersed oil (both that oil dispersed by the intense turbulence of the release conditions and the enhanced dispersion caused by subsea dispersant addition) was detected by fluorimetry as a dilute plume of dispersed oil at a water depths of between 900 m and 1300 m, i.e. 200 m to 600 m above the oil and gas release. The readings were highest near the release site, generally decreasing with distance, and trending primarily southwest to northeast consistent with the measured water current (JAG, 2010a).

The Joint Analysis Group (JAG) "Review of Subsurface Dispersed Oil and Oxygen Levels Associated with the Deepwater Horizon MC252 Spill of National Significance" (JAG, 2012) report concluded:

- The oil that was detected was classified into volatile fraction hydrocarbons (partly water soluble) and semi-volatile fraction hydrocarbons. Separately reporting these two classes of hydrocarbons allowed differences in the fate of these fractions observed early in the spill to be distinguished. Some evidence shows that the most easily biodegraded fractions of the oil, the volatile fraction hydrocarbons, were preferentially consumed.
- The observed decreases in hydrocarbon concentrations with increasing distance from the wellhead were likely due to multiple factors, primarily dilution and biodegradation; other factors, such as particulate adsorption, could have also contributed to the decreases.
- The highest concentration of volatile hydrocarbons detected in water between the depths of 900 m and 1,300 m was 2,112 parts per billion (ppb) found in a sample 1.2 km from the wellhead. Beyond 20 km from the wellhead, volatile hydrocarbon concentrations were below 100 ppb and values beyond 100 km from the wellhead were below analytical method detection levels.

The levels of semi-volatile fraction hydrocarbons at depths between 900 m and 1,300 m were primarily in the 1–10 ppb range at distances of >10 km from the well. The highest volatile hydrocarbon level in a water sample was 485 ppb also found in a sample 1.2 km from the wellhead. Measurable amounts of semi-volatile hydrocarbons were found 400 km from the wellhead; values above 10 ppb were found out to about 275 km..

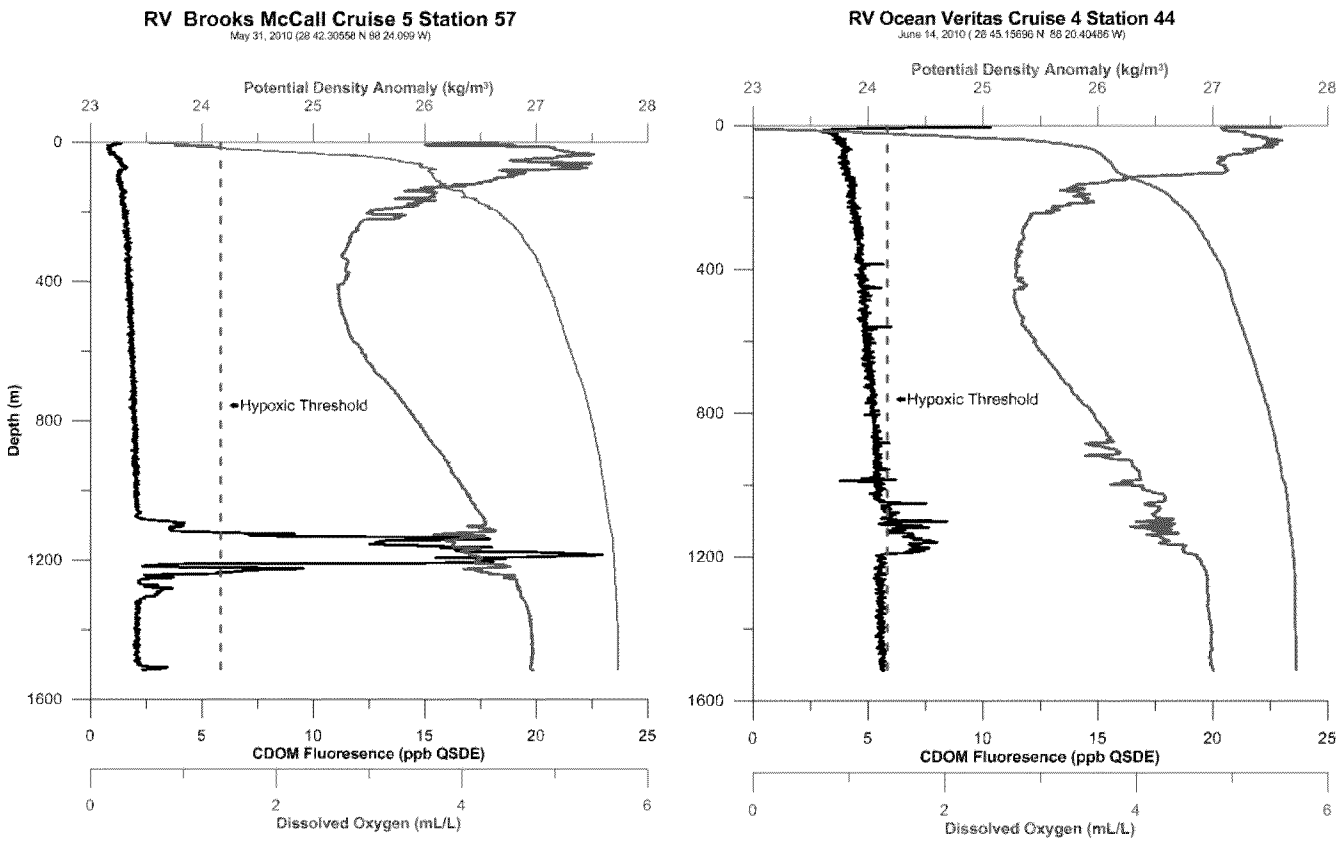


Figure X: Two examples of the many measurements made during monitoring of the water column

Dissolved Oxygen measurements

The dissolved oxygen content of the water was depleted to some degree in the vicinity of the dispersed oil plume, but the subsea dispersant operation did not create any oxygen-depleted zones that would harm the marine organisms. The dissolved oxygen content of the water never dropped below the ecologically significant threshold of 2.0 mg/l.

Water column sampling and analysis results

Water samples were collected in the locations where fluorimetry had indicated the highest dispersed oil concentrations and these water samples were analysed for specific hydrocarbons.

Human health benchmarks

Human health benchmarks developed by the EPA in coordination with the Department of Health and Human Services are used to assess potential human health risks from exposure to oil-contaminated water. The benchmark consists of screening levels for a number of compounds, including volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAHs) and metals.

A total of 11,634 (6,090 nearshore, 750 offshore and 4,794 in deep water) samples were analysed for comparison to the Human health benchmark. None of samples exceeded the EPA benchmark.

Aquatic life benchmarks

The EPA established benchmark 'levels of concern' for PAH concentrations in water and sediment to screen for potential adverse impacts to aquatic life. The water samples were analysed for a total of 41 oil chemical compounds, including 7 volatile organic compounds, 16 parent PAHs and 18 alkylated homologues of the parent PAHs. Each of the individual chemical compounds were assigned a potential toxicity so that the cumulative toxicity (acute or chronic) of the mixture of compounds in each s ample

could be calculated. These aquatic life benchmarks were established on the basis of a suite of laboratory toxicity evaluations using contaminated water and various species, life stages, endpoints, and exposure durations.

A total of 10,578 (6,090 nearshore, 749 offshore and 3,739 in deep water) samples were analysed for comparison to the Aquatic life benchmark. 111 (approximately 1% of the total) samples, with 1% from sediment locations and <1% from water locations, and confirmed as being due to the crude oil released from the well, exceeded the EPA benchmark.

Dispersant benchmarks

The water samples were analyzed for four dispersant constituents:

- 2-Butoxyethanol
- Dipropylene Glycol n-Butyl Ether (DPnB)
- Propylene Glycol
- Dioctylsulfosuccinate (DOSS)

Benchmarks, based on dissolved seawater concentrations for the individual compounds, were used to establish "levels of concern" based on available biological effects data and were conservatively designed to protect aquatic life.

A total of 10,178 (5,262 nearshore, 682 offshore and 4,334 in deep water) samples were analyzed for comparison to the Dispersant benchmark. Only 16 (0.3 percent) exceeded the EPA aquatic life benchmarks for dispersant chemicals.

Toxicity testing

Laboratory testing done using the standard Rototox™ protocols and Macondo crude oil dispersed with Corexit 9500A indicated that the LC_{50} value for the rotifer, *B. plicatilis* was in the range of 10 to 17 ppm. The highest observed total petroleum hydrocarbons (TPH) values in the field where toxicity tests were conducted were considerably less than this. It is therefore not surprising that no signs of toxic response were revealed in the Rototox™ toxicity testing conducted as Part 2 of the required water column monitoring.

In addition, toxicity tests were also conducted on various benthic and pelagic species:

Sample type	Test type	Duration	Endpoint	Number of tests
Water	Fish	96 hours	Survival	126
		7 days	Survival, Growth, Biomass	36
	Mysid shrimp	96 hours	Survival	93
		7 days	Survival, Growth, Fecundity, Biomass	30
	Pink shrimp	7 days	Survival	88
	Sea Urchin	120 minutes	Fertlization	2
	Mollusc	48 hours	Survival, Embryo development	20
	Diatom	96 hours	Growth	68
	Algae	96 hours	Growth	68
Sediment	Amphipod	96 hours	Survival, Growth	74
		10 days	Survival, growth, Reburial	505
	Worm	10 days	Survival	112
	Mysid	48 hours	Survival	256
		96 hours	Survival, Growth	65
	Sea Urchin	60 minutes, 48 hours	Fertilization, Embryo Development	66

A total of 3,548 toxicity tests were conducted during the spill and the associated response, making it the most extensive testing programme ever conducted to characterize the effects of an oil spill in the marine environment. 90 percent of the tests results showed no statistically significant effects. None of the concentrations of dispersant related constituents found in the sediment and water samples collected after Aug. 3, 2010 in the nearshore zone exceeded EPA's chronic aquatic benchmarks. (OSAT, 2011).

Addressing the concerns over sea food

To address concerns about the potential effect of oil and dispersants on seafood, in June 2010, the National Oceanic Atmospheric Administration (NOAA) and the US Food and Drug Administration (FDA), in consultation with the EPA and the Gulf states, agreed to an extensive sampling and testing procedure. Areas once closed to fishing were reopened only when all seafood sampled in the area passed both the established sensory and chemical testing. While initial testing was focused on oil contaminants, in October 2010, the FDA and NOAA created a new test that could detect traces of dispersant constituents in fish tissue. (US FDA, 2010). Every sample tested was well below FDA levels of concern, with 99 percent of the samples showing no detectable residue

To date, none of the seafood tested by the FDA, NOAA and the Gulf states has exceeded the FDA's human health thresholds. Gulf of Mexico seafood is among the most rigorously tested sources of seafood on the US market. Since May 2010, the Food and Drug Administration (FDA), NOAA and the Gulf states have tested more than 10,000 finfish and shellfish specimens and levels of PAHs in seafood consistently have tested 100 to 1,000 times lower than FDA safety thresholds (US FDA, 2012).

Natural Resource Damage Assessment (NRDA)

The US Oil Pollution Act of 1990 addresses environmental impacts from a spill through two mechanisms:

- **Response** - Actions taken to contain and remove oil from the water and shoreline and minimize damage to the public health and welfare.
- **Restoration** - Actions taken to restore or replace injured natural resources and compensate the public for temporary lost use of those resources.

To begin to understand the environmental impact, scientists were in the field within days of the accident to evaluate the potential for injury to wildlife and habitats, as well as lost recreational use of these resources. This was the start of Natural Resource Damage Assessment (NRDA) – the largest such environmental assessment ever performed. By early 2015, NRDA scientists have conducted more than 240 studies including investigations of potential benthic impacts. These assessments are still underway.

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Part Three: Operational Aspects

Operational Overview

The basic operations of subsea dispersant use are:

- A surface vessel is used to transport a supply of dispersant and the required application equipment to the site of the subsea oil release.
- The equipment is deployed and, if possible, subsea monitoring is conducted to characterize the subsea oil release.
- Dispersant is pumped from the surface to a subsea manifold. A jumper from the manifold is connected to a nozzle held by a remotely operated vehicle (ROV) located close to the release.
- The ROV positions the nozzle to directly inject dispersant into the flow of oil or as close to the release point as possible.
- Dispersant is pumped at a controlled rate from the deck of the surface vessel through the nozzle and into the oil.
- The subsea dispersant use is monitored to assess whether it is being effective and to provide information about the locations of dispersed oil plumes in the water column and the poten tial to toxic effect to be caused to marine organisms.

Equipment required

The first step is to mobilize the necessary equipment to well source control location.

Resource Type	Specific Equipment, Supplies or Other Items
Vessel	Offshore Construction Vessel to transport and deploy subsea dispersant injection system and initial dispersant supply shuttle vessel(s) to transport restock dispersant supply
Chemical Supplies	Dispersant
Operating Equipment	Multiple ROVS to assist in installation / operation Coil tubing unit Subsea manifold Dispersant pumping system Vessel-to-vessel hose and equipment for refilling dispersant storage tanks
Subsea Dispersant Monitoring Kit	Research vessel Specialized instrumentation for conducting monitoring of subsea dispersant injection operation Science team to support monitoring operation
Procedures	Installation / operation procedures customized for the responder's vessel(s)
Planning/Procedures	Dispersant deployment plan (ISO tanks to vessel) Dispersant injection plans (ratio of oil flow to dispersant injection or DOR) Transfer plan for restocking pumping operations Dispersant monitoring planning Contingency planning for installation
Planning	Staging / sequencing plan for arrival of dispersant tanks at shore base Ensure vessel charter agreements include dispersant
Agreements	Agreement with dispersant supplier to purchase additional dispersant

Table x. Example preparedness checklist for Subsea Dispersant Injection (Courtesy of MWCC).

Dispersant stockpiles

Dispersant stockpiles are maintained worldwide as part of Oil Spill Response Limited's Global Dispersant Stockpile (GDS) of 5,000 m^3 (or 5 million litres) of dispersant. The stockpiles are positioned to enable quick access to dispersants and ensure sufficient stock can be mobilized for an individual spill response incident. Access to the GDS is available to all OSRL's members who sign the GDS supplementary

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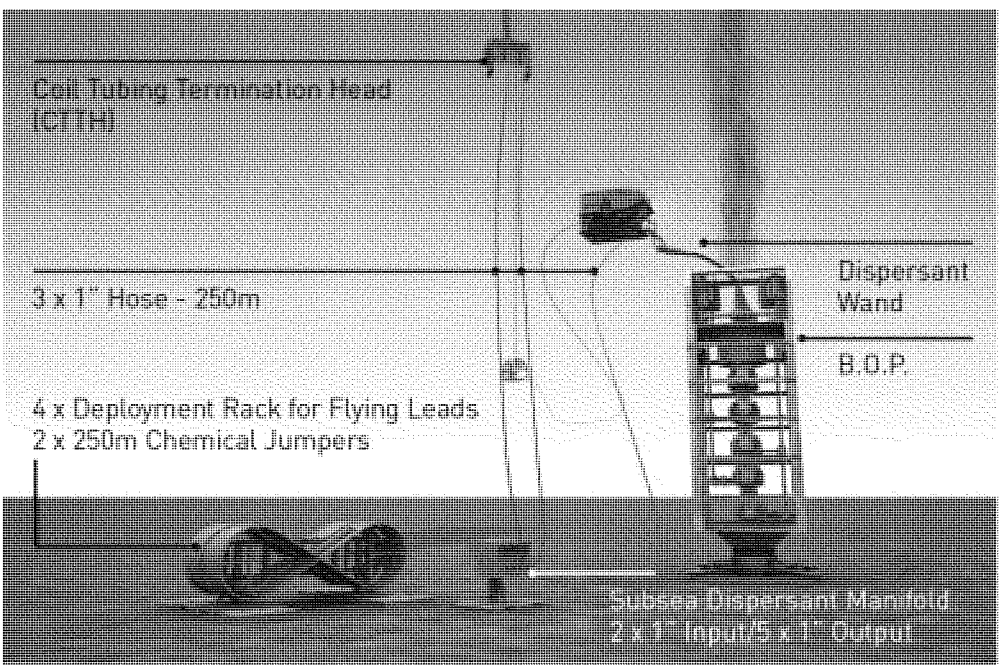
agreement. Other response organizations such as the Marine Well Containment Company (MWCC) in the Gulf of Mexico and the Australian Marine Oil Spill Centre (AMOSC) in Australia have also developed site-specific dispersant stockpiles.

Deployment of SSDI equipment

Once the SSDI equipment arrives on-scene at the source-control area, the dispersant supply vessel is positioned on the surface above the wellhead. Due to other operations that may be occurring near well head (e.g., cap and containment activities, debris removal, relief well drilling, etc.), all vessels and activities must be carefully coordinated through a central command system known as Simultaneous Operations command (SIMOPS). SIMOPS exists to coordinate all activities on the ocean surface and subsea to ensure the safety of all vessels that are operating in close proximity.
After the vessel is in position, surface dispersant hoses are attached to the dispersant supply tanks. Then the dispersant manifold and clump weights with the coiled tubing are deployed from the vessel. Remotely Operated Vehicles (ROVs) are used to connect the various components of the subsea dispersant injection system.



The SWIS Subsea First Response Toolkit (Source: SWRP/SWIS)

Once fully assembled and checked, the ROV then inserts the dispersant applicator (or application wand) into the flowing oil plume. A second ROV would assist the first ROV by providing lighting and video surveillance at the sea floor. Once the application wand is in position, dispersant pumping will be initiated from the dispersant vessel. The pumping rate and dispersant operation will be adjusted to maximize dispersant effectiveness, as indicated by in situ operational monitoring.

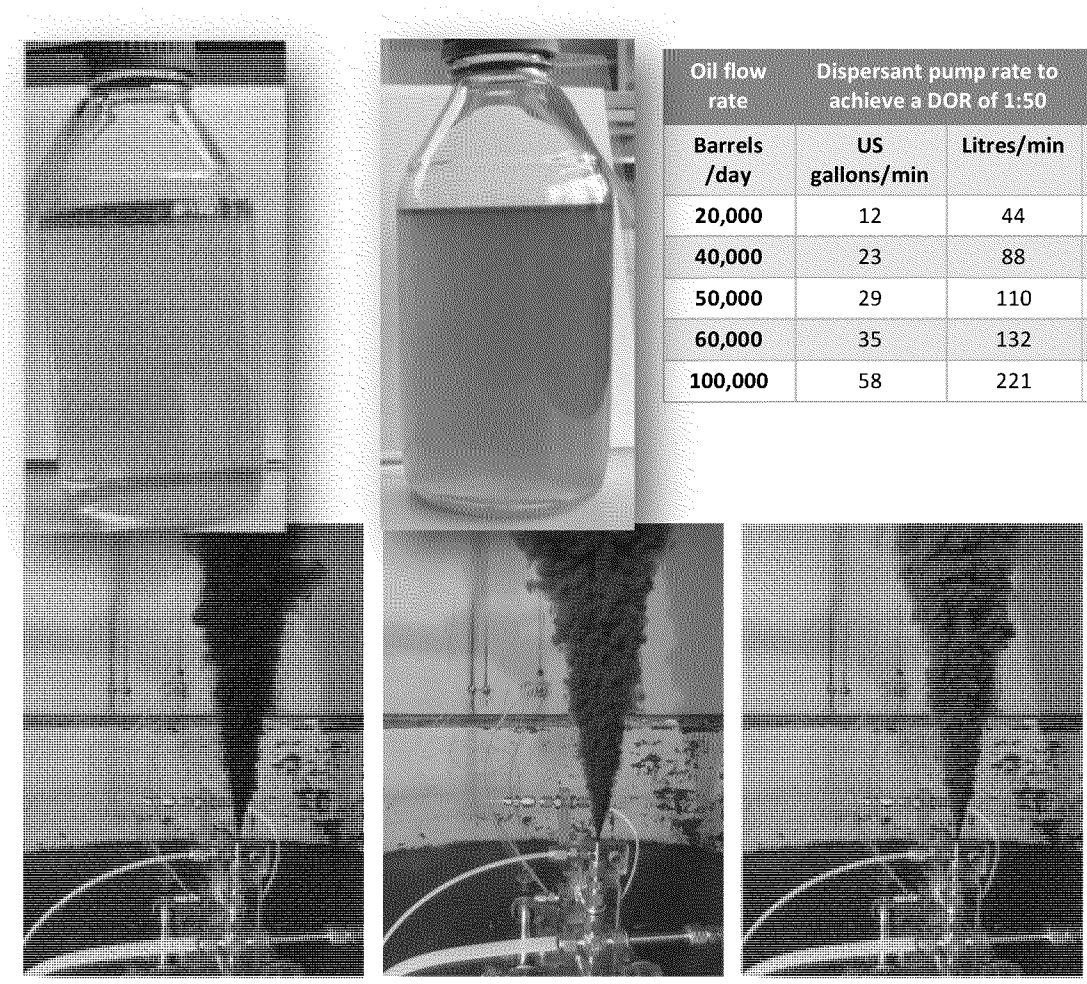
The mobilization and assembly time described here would likely take several days. Once operational, however, the system can be sustained 24 hours per day since it is not constrained by daylight or anything but extreme surface weather. Even then, it may be possible to deploy a self-contained dispersant pumping system to the seafloor that could operate without any human intervention from the surface. One such system was developed by MWCC and is known as the Subsea Autonomous Dispersant Injection (SADI) system. The SADI system could be used to provide SSDI in the event that an emergency site evacuation of personnel was needed. It consists of a dispersant storage bladder, manifold and injection pump system that can be self-powered at the seafloor without any surface vessel support.

Required subsea dispersant treatment rate

The dispersant treatment rate will depend on the precise circumstances of the oil release. The rate is most often expressed as a Dispersant to Oil Ratio (DOR), being the required dispersant to produce a significant increase in the proportion of oil droplets that are small enough to be retained in the water column.

As noted in a previous section, it is not possible to know the subsea DOR that was used at the *Deepwater Horizon* incident because the oil and gas flow rates were not known with any degree of accuracy.

Subsequent research (Brandvik et 2014) using scaled-down oil and gas releases has indicated that DORs of 1:50, 1:100 or less may be sufficient to cause substantial additional dispersion. During an incident the DOR would be based on observations from field monitoring. The dispersant pumping rate would be adjusted to achieve the minimum DOR needed for effective dispersion at the prevailing oil flow rate.



Oil flow rate	Dispersant pump rate to achieve a DOR of 1:50		Dispersant pump rate to achieve a DOR of 1:100	
Barrels /day	**US gallons/min**	**Litres/min**	**US gallons/min**	**Litres/min**
20,000	12	44	6	22
40,000	23	88	12	44
50,000	29	110	15	55
60,000	35	132	18	66
100,000	58	221	29	110

Oseburg crude oil with no Corexit 9500 dispersant (left), DOR of 1:100 (middle) and 1:50 (right). The jars show the sampled water with no dispersant and DOR of 1:100. Graph shows the reading of droplet size with no dispersant and DOR of 1:100.

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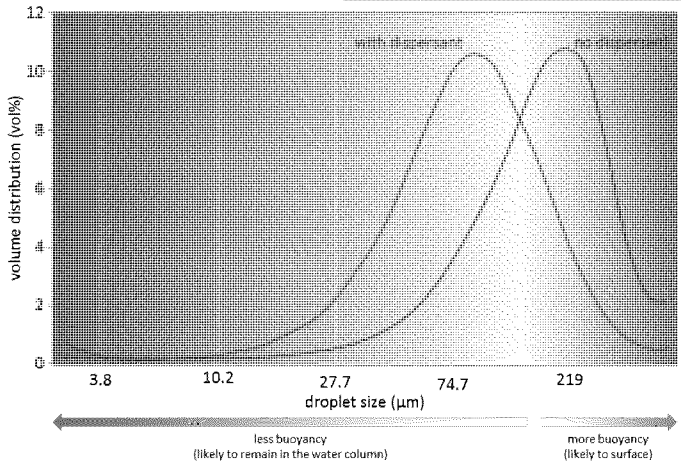

Monitoring of a subsea dispersant operation

SSDI, like all response techniques, is likely to be less than 100% effective and some of the oil may rise to the surface where more traditional oil spill monitoring techniques, such as the use of the SMART (Special Monitoring of Applied Response Technologies) protocols, can be used. Subsea monitoring programmes, therefore, will likely be implemented in conjunction with surface oil monitoring programmes.

The API has developed guidance for industry that is concerned primarily with operational monitoring (API, 2013). Its focus is to collect real-time or near real-time monitoring data that can be used to inform operational decisions for the current day or the next day. Monitoring data that takes days to collect and analyse does not support operational decision-making. This guidance groups monitoring activities into three phases which address:

- Assessment of subsea dispersant use effectiveness;
- Characterization of the nature and extent of subsea, or near surface, dispersed oil plumes; and
- An initial assessment of potential ecological effects as they relate to operational response decision-making.

These phases are initiated in the order listed, but each phase is based on information produced by the one that preceded it. Each phase is intended to be implemented on a time line that parallels the deployment of subsea dispersant injection resources during the response phase.

Phase 1: Assessment of subsea dispersant effectiveness

The initial question that must be answered by the subsea monitoring program is "Is SSDI likely to be effective?"

Initially, monitoring at the release point is required to characterize the nature of the subsea oil release, estimate the oil and gas flow rates, and determine the properties and behaviour of the released oil. This information serves as pre-dispersant application background data and is used to guide selection of dispersant injection methods and application rates.

Assessment of dispersant effectiveness can be estimated by comparing baseline data, collected prior to dispersant application, (i.e., visual appearance, air and water quality data) with data collected after initiation of dispersant application. Dispersant effectiveness can be assessed:

- Visually, by examining the output from video cameras on ROVs to assess whether the shape or colour of the oil discharge changes with dispersant addition.
- Acoustically, by analysing backscatter data generated from a ROV-mounted sonar. Sonar imaging of the jet of oil before and after dispersant injection can also give an indication of dispersant effectiveness. This is because sonar at the appropriate wavelength should give a strong backscatter signal prior to injection of dispersant and a much weaker backscatter signal after injection.

- Visually, by analysing the area of oil on the sea surface in aerial photographs. Aerial photography should be conducted before and during the subsea injection of dispersant to determine if the use of dispersant is reducing the amount of oil reaching the surface.
- By air monitoring for VOCs and percentage Lower Explosive Limit (LEL) on vessels in close proximity to the well site before and after dispersant addition.

None of these techniques taken individually can directly quantify dispersant effectiveness, but collectively, the data produced can provide sufficient evidence to support operational decisions to continue or modify dispersant use. Note that changes in surface expression of the oil will take time to express depending on surface winds / currents and the expected rise time of oil through the water column.

Phase 2: Characterize the nature and extent of subsea, or near surface, dispersed oil plumes

Once it is assessed that SSDI is being effective, the next phase of monitoring seeks to define the magnitude and behaviour of subsea dispersed oil plumes. The purposes of this monitoring phase are to:

- Determine the location, extent, and characteristics of the dissolved and dispersed oil within the water column;
- Characterize the lateral and vertical movement of the dissolved and dispersed oil; and
- Document changes in the concentration of oil as it moves away from the source.

Local oceanographic data together with hydrodynamic models, if available, will determine the likely direction of movement of the sub-surface oil.

Water column monitoring

The primary monitoring strategy involves using a research vessel outfitted with an A-frame and winch to conduct sampling casts using a Conductivity Temperature Depth (CTD) instrument and Rosette sampler (see Figure x). The CTD is outfitted with a fluorimeter, dissolved oxygen sensor, and a deep-water laser light scattering particle size analyser (e.g., LISST).

Using this strategy, water samples are collected and stored for subsequent detailed chemical analysis from depths determined by the results of the CTD casts for selected stations. Water samples for shipboard dissolved oxygen measurements should be collected at depths above, in and below any observed increase in fluorimetric response.

A laser light scattering particle size analyser provides real-time in situ measurements of the dispersed oil droplet size distribution. A significant shift from larger to smaller droplets sizes are indicative of dispersion of the oil.

Water sampling

The determination of water sampling site locations should be based on information from a reliable 3-D subsea oil spill model. If no such models are available, a sampling grid should be developed and centred on the spill location. Stations should be established in a radial pattern moving out from the centre, and fluorimeter readings from CTD casts and light scattering measurements should be used to determine the path of the dispersed oil.

Following retrieval of the instruments, the water samples should be transferred into suitable containers and stored until subsequent analysis.

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Phase 3: Initial assessment of potential for ecological effects

This phase of monitoring seeks to fully characterize all water samples collected by CTD casts, using state-of-the-art laboratory analytical techniques for petroleum analytes and dispersant marker analysis. Once water samples are collected, they must be returned to land for rapid transfer via to a certified, accredited laboratory utilizing appropriate chain-of-custody procedures. Depending on the incident location, vessel transit time, sample transfer time, and laboratory processing can equate to a minimum of five days to process a sample. In the case of a larger spill event where significant numbers of samples are collected, it could take at least 7-10 days to receive detailed analytical results that have met quality assurance and control (QA/QC) standards. It is very unlikely that many locations in the world would have sufficient laboratory facilities to sustain the level of toxicology and analytical chemistry required during the water sampling and monitoring phase of the dispersant response to the Deepwater Horizon incident.

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Conclusion

The reason for using dispersants, either on floating oil or by subsea use, is the same; to minimize the overall ecological and socio -economic damage, by preventing the released oil from drifting into nearshore or coastal habitats and onto the shore. Dispersant use on floating oil transfers the oil from the sea surface and into the upper layer of the water column. Subsea dispersant use aims to prevent the oil released subsea from reaching the sea surface by dispersing the oil into the water close to the release. This provides a major health and safety benefit by greatly reducing the exposure of personnel responding near the release site to volatile organic compounds (VOCs).

The experience of subsea dispersant use gained at the *Deepwater Horizon* incident in 2010 has shown that SSDI can be an effective response technique for subsea oil and gas blowouts. More oil would have come ashore if subsea dispersant use had not been undertaken. The challenges of conducting a response to oil released 5,100 feet (1,550 m) below the sea surface with a technique that had never been used before were great. Considerable ingenuity and expertise were required to develop subsea dispersant injection (SSDI) into a viable response during the largest oil spill response ever conducted.

As a response to a subsea oil release, SSDI has many advantages over the strategy of respond ing to the released oil only when it reaches the sea surface. Using SSDI:

- Treats all the oil released at the point of release;
- Uses less dispersant compared to surface application;
- Reduces the exposure of responders to VOCs and oil;
- Can be conducted continuously, day and night and in practically any weather conditions, unlike response techniques on the sea surface.

Dispersing released oil into the water column has capabilities and limitations plus potential benefits and drawbacks that, like the consideration of any response technique, need to be addressed by conducting NEBA (Net Environmental Benefit Analysis). The addition of dispersant will cause more of the released oil to be produced as the smaller oil droplets that will be retained within the water column. SSDI use has benefits:

- Dispersing the released oil into the water column prevents the oil from reaching the sea surface from where it could drift ashore causing severe and long-lasting damage to oil-sensitive coastal habitats and disrupt socio-economic activities.
- Dispersing the oil into the water as small oil droplets permits rapid colonization by petroleum degrading microorganisms that naturally occur in ocean environments. These microorganisms will substantially biodegrade the majority of the oil within days and weeks. The dispersant will also be biodegraded.

However, increasing the amount and concentrations of dispersed oil in the water increases the risk to marine organisms of toxic effects caused by exposure to dispersed oil, but only from the already high levels that will occur at high-velocity, high- flow rate oil and gas blowouts. The trade-offs involved in using SSDI need to be understood by all concerned and, ideally, should be addressed during contingency planning.

The logistics of conducting SSDI require considerable specialist equipment, trained personnel and support. Multiple ROVs will be required with dedicated offshore supply vessels. Subsea dispersant use requires subsea monitoring to assess whether it is being effective and whe re the subsea plumes of oil would be transported by the prevailing deep water currents. In order to address concerns about the possibility of toxic effects being caused to marine organisms by the dispersed oil, it may be necessary to conduct extensive water monitoring and water-sampling surveys with subsequent chemical analysis and toxicity testing. This was done at the *Deepwater Horizon* incident. Concerns about substantial toxic

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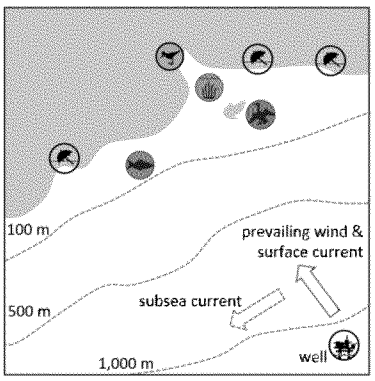
effects to marine organisms, oxygen depletion in the water due to biodegradation and the persistence of dispersant in the water column were not borne out by the measurements made.

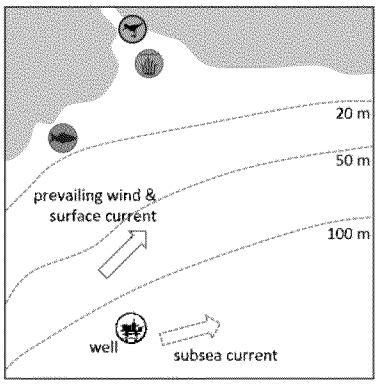
Annex 1: Outline of NEBA for three subsea release planning scenarios



An exploration well suffers loss of control including failure of the blowout preventer. Crude oil and gas are released, with the oil estimated to be flowing at 3,000 m³ (19,000 bbls) per day.

- The well is in 1,100 m water depth.
- Surfacing oil slicks are drifting towards the shore under the influence of a prevailing 15 knot wind and surface current.
- Subsea current runs parallel to the coast
- Wave height is around 1.5 m.
- There are fishing grounds closer to the coast and seagrass beds in shallow water.
- Coastal resources that could be impacted by the oil include an estuarine mud-flat that supports a large population of wading birds. An offshore island supports a seabird colony. There are three popular tourist resorts in the vicinity.

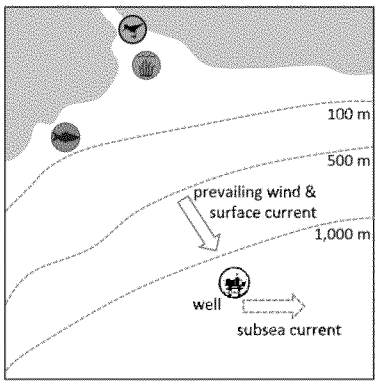
Summary of NEBA	
Evaluate data	With no intervention and under prevailing conditions, modelling predicts an 80% probability that surfacing spilled oil would reach the shore, with oil reaching the coast after four days. During this time the spilled oil would become progressively 'weathered' and emulsified. The spilled oil volume would initially decrease due to evaporative loss, but then increase due to emulsification. This could result in up to 10,000 m³ per day of emulsified oil threatening the coast after four days. Gas released within the well fluids would dissolve before reaching the surface.
Predict outcomes	The near shore and coastal sensitivities are very high and their protection from oil would result in high environmental benefit. The estuarine mud-flat is biologically productive and difficult to either protect with booms or clean-up if oiled. The seabird colony does not contain threatened species but adds to the attraction of the area for tourists, with daily boat trips. The tourist resorts are a major part of the regional economy, relying on popular sandy beaches and watersports. The tourism is seasonal but this scenario falls within the main season. The threat to beaches would cause significant immediate disruption and has the potential to dent confidence in the area and reduce future reservations. The inshore fishery is locally important but economically small in relation to tourism.
Balance trade-offs	At sea mechanical recovery or in-situ burning alone could not deal with the amount of spilled oil in the time available. Surface use of dispersant is possible; the crude oil is tested to be amenable to dispersant use prior to emulsification, with a window of opportunity of around 24 hours. The prevailing conditions of 1.5 metres wave height and 15 knot wind are good for dispersant use. However the surfacing oil would rapidly spread and fragment, presenting challenges for targeting and encountering the floating oil even using a combination of vessels and aerial systems. Approximately 150 m³ of dispersant would need to be applied each day, based on dispersant to oil ratio (DOR) of 1:20. An aerial application system is available within 24 hours, capable of applying up to 100 m³ of dispersant per day. First response is available from a standby vessel with boat spray system and stock of 5 m³ of dispersant. Mobilizing a subsea dispersant infection system as part of a capping system would allow treatment to commence within seven days, with dispersant supplied from the global stockpile. Injection at the wellhead would greatly increase both the targeting of the dispersant operation and the volume of oil surfacing. The DOR could be decreased to 1:50 or less, reducing the volume of dispersant used per day by more than 50%. Surface dispersant application could then be scaled down or stopped. The enhancement of subsea dispersed oil through dispersant injection would pose a heightened risk to pelagic marine life, primarily within a few kilometres of the well location. However dilution of dispersed oil would (i) reduce concentrations to below toxicity levels in the wider area, (ii) enhance biodegradation and (iii) greatly mitigate gross oiling of the sensitive coastal zone. It is anticipated that the well would be capped within 15 days.
Select best options	Initial surface dispersant use on the floating spilled oil, followed by subsea injection as soon as it can be mobilized, would be effective and be the primary response tool. Inshore containment and recovery operations would be mobilized and targeted around the ecologically sensitive areas. Shoreline cleanup would be carried out around the sandy tourist beaches.



An exploration well suffers loss of control including failure of the blowout preventer. Crude oil and gas are released, with the oil estimated to be flowing at around 3,000 m³ (19,000 bbls) per day.

- The well is in 130 metres water depth.
- Surfacing oil slicks are drifting towards the shore under the influence of a prevailing 10 knot wind and surface current.
- Subsea current runs parallel to the coast.
- Wave height is around 0.5 m.
- There are fishing grounds closer to the coast and seagrass beds in shallow water.
- Coastal resources that could be impacted by the oil include an estuarine mud-flat that supports a large population of wading birds.

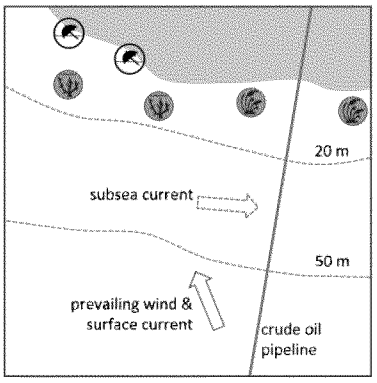
Summary of NEBA	
Evaluate data	With no intervention and under prevailing conditions, modelling predicts a 95% probability that surfacing spilled oil would reach the shore, with oil reaching the coast after approximately 2 days. During this time the spilled oil would become progressively 'weathered' and emulsified. The spilled oil volume would initially decrease due to evaporative loss, but then increase due to emulsification. This could result in up to 10,000 m³ per day of emulsified oil threatening the coast after 2 days.
Predict outcomes	The near shore and coastal sensitivities are high and their protection from oil would result in high environmental benefit. The estuarine mud-flat is biologically productive and difficult to either protect with booms or clean-up if oiled. The inshore fishery is locally important.
Balance trade-offs	The gas included in the well fluids would not have time to fully dissolve and would surface at the well site. This would severely restrict operations in the vicinity of the site due to safety concerns. Surface pollution response would be limited to sea areas away from the site. At sea mechanical recovery or in-situ burning alone could not deal with the amount of spilled oil in the time available. Surface use of dispersant is possible; the crude oil is tested to be amenable to dispersant use prior to emulsification, with a window of opportunity of around 24 hours. The prevailing conditions of 0.5 metres wave height and 10 knot wind are good for dispersant use. However the surfacing oil would rapidly spread and fragment especially under the influence of gas within the well fluids, presenting challenges for targeting and encountering the floating oil even using a combination of vessels and aerial systems. Approximately 150 m³ of dispersant would need to be applied each day to treat all the oil, based on dispersant to oil ratio (DOR) of 1:20. An aerial application system is available within 24 hours, capable of applying up to 100 m³ of dispersant per day. First response is available from a standby vessel with boat spray system and stock of 5 m³ of dispersant. Spraying would be allowed up to the 20 m depth contour in line with national regulations. Mobilizing a subsea dispersant infection system may be delayed or restricted by the presence of gas at the surface. Specific assessments would be carried to investigate the feasibility of deploying a subsea injection system. If it was considered feasible, injection at the wellhead would greatly increase the targeting of the dispersant operation and reduce by a large amount the volume of oil surfacing as the DOR could be decreased to 1:50 or less. It could also lead to a reduction in the volume of dispersant used per day by more the 50%. In this circumstance, the gas lift may bring dispersed oil into the well-mixed turbulent surface waters, rather than creating a subsea plume. Surface dispersant application could then be greatly scaled down or stopped. The enhancement of subsea dispersed oil through dispersant injection would pose a heightened risk to pelagic marine life, primarily within a few kilometres of the well location. Dilution of dispersed oil would (i) reduce concentrations to below toxicity levels in the wider area, (ii) enhance biodegradation and (iii) greatly mitigate gross oiling of the sensitive coastal zone. Depending on circumstances, the well would either be capped within 15 days or the flow stopped when a relief well could be drilled.
Select best options	Initial surface dispersant use on the floating spilled oil, followed by subsea injection if it can be safety mobilized and deployed, would be an effective part of the response. Inshore containment and recovery operations would be mobilized and targeted around the ecologically sensitive inlet. As this is remote area after from major population and habitations, inshore in-situ burning would be mobilized. Shoreline clean-up options would be considered in the light of the extent and type of coastal habitats affected.



An exploration well suffers loss of control including failure of the blowout preventer. Crude oil and gas are released, with the oil estimated to be flowing at around 2,000 m³ (12,500 bbls) per day.

- The well is in 1,200 m water depth.
- Surfacing oil slicks are drifting away the shore under the influence of a prevailing 20-25 knot wind and surface current.
- Subsea current runs parallel to the coast
- Wave height is around 2.5 m.
- There are fishing grounds closer to the coast and seagrass beds in shallow water but these are currently not being threatened.
- However, coastal resources that could be impacted by the oil if the wind changed direction include an estuarine mud-flat that supports a large population of wading birds. An offshore island supports a seabird colo ny. There are three popular tourist resorts in the vicinity.

Summary of NEBA	
Evaluate data	With no intervention and under prevailing conditions, modelling predicts a 0% probability that surfacing spilled oil would reach the shore. The modelling predicts that a significant proportion of the subsea release will naturally disperse. Furthermore, surfacing oil will break-up and dissipate under the prevailing rough sea conditions resulting in only transient surface oil slicks. Gas released within the well fluids would dissolve before reaching the surface.
Predict outcomes	The near shore and coastal sensitivities are very high and their protection from oil would result in high environmental benefit. However the current prevailing weather c onditions indicate that the coastal resources are not under immediate threat of oiling.
Balance trade-offs	Prevailing rough sea conditions would preclude the use of any on-water containment techniques (mechanical recovery and in-situ burning), leaving subsea dispersant injection and surface dispersant application as the only viable active response options to treat any floating oil. The current predictions are for continuing offshore prevailing winds between 20-25 knots for the next 3-5 days. Modelling indicates that this will continue to break up any surfacing oil, without the formation of persistent slicks.
Select best options	Aerial surveillance and monitoring of the offshore area around the release is required to assess and verify modelling predictions, including the rapid dissipation of any surfacing oil slicks. The mobilization to a standby condition of subsea dispersant injection and surface application capability would be undertaken as a precaution. The dispersant option would only be utilized if the weather abated to the extent that observed persistent surface slicks began to form. Initial preference would then be to inject dispersant subsea, in order to provide the most efficient means to reduce or prevent oil from reaching the surface. Continual monitoring of the 5-10 day weather forecast would inform any decisions to mobilize other response tools, including offshore containment systems and shoreline protection capability. However the locality has persistent offshore winds during the sea son in which this incident has occurred, therefore these resources are considered unlikely to be needed in the medium term.



A crude oil pipeline suffers damage due to a vessel dragging its anchor. The line is shutdown but oil is detected on the sea's surface

- The incident occurs in 50 m water depth.
- Surfacing oil slicks are drifting towards the shore under the influence of a prevailing 10 knot wind and surface current.
- Subsea current runs parallel to the coast.
- Wave height is around 0.5 m.
- There are mangroves along the coast and tourist resorts with offshore coral reefs to the west.

Summary of NEBA	
Evaluate data	With no intervention and under prevailing conditions, modelling predicts a 9 8% probability that surfacing spilled oil would reach the shore, with oil reaching the coast after approximately 24 hours. During this time the spilled oil would become progressively 'weathered' and emulsified. The spilled oil volume would initially decrease due to evaporative loss, but then increase due to emulsification. The maximum volume in the pipeline is approximately 2,000 m^3.
Predict outcomes	The coastal ecological sensitivities are high and their protection from oil would result in high environmental benefit. The mangroves are biologically productive and difficult to either protect with booms or clean-up if oiled. The tourist reports are luxury style and rely heavily on pristine beaches and scuba diving clientele.
Balance trade-offs	Depending on the extent of pipeline damage, an initial release of oil would be expected to be followed by lower volume leakage. Preference would be given to inshore mechanical recovery and systems would be mobilized. Surface use of dispersant is possible; the crude oil is tested to be amenable to dispersant use prior to emulsification. The prevailing conditions of 0.5 metres wave height and 10 knot wind are good for both recovery and dispersant use. An aerial application system is available within 6 hours, capable of applying up to 15 m^3 of dispersant per day. Spraying would be allowed up to the 20 m depth contour and more than 2 km away from coral reefs in line with national regulations. Mobilizing a subsea dispersant infection system would not be feasible, as there is no suitable subsea mixing energy from such a pipeline release.
Select best options	Initial surface dispersant use on the floating spilled oil would provide the most rapid response and provide the best option for protection of the critically important mangrove habitat. This would be supported the use of mechanical recovery operations inside the 20m contour. Preparations would be made for clean-up of tourist resort beaches where appropriate.

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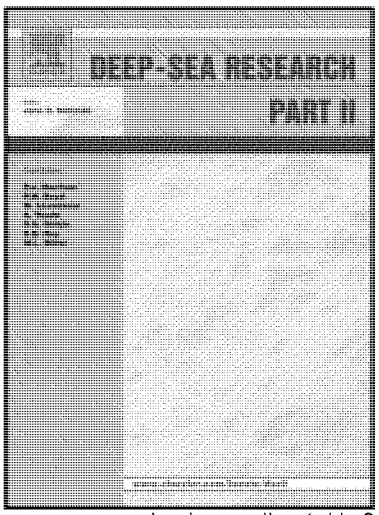

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Response of deep-water corals to oil and chemical dispersant exposure

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Response of deep-water corals to oil and chemical dispersant exposure

Abstract

Cold-water corals serve as important foundation species by building complex habitat within deep-sea benthic communities. Little is known about the stress response of these foundation species yet they are increasingly exposed to anthropogenic disturbance as human industrial presence expands further into the deep sea. A recent prominent example is the Deepwater Horizon oil-spill disaster and ensuing clean-up efforts that employed chemical dispersants. This study examined the effects of bulk oil-water mixtures, water-accommodated oil fractions, the dispersant Corexit9500A®, and the combination of hydrocarbons and dispersants on three species of corals living near the spill site in the Gulf of Mexico between 500-1100 meter depths: *Paramuricea sp. B3, Callogorgia delta* and *Leiopathes glaberrima*. Following short-term toxicological assays (0 – 96 hrs), all three coral species examined showed more severe health declines in response to dispersant alone (2.3 – 3.4 fold) and the oil-dispersant mixtures (1.1 – 4.4 fold) than in the oil-only treatments. Higher concentrations of dispersant alone and the oil-dispersant mixtures resulted in more severe health declines. *C. delta* exhibited somewhat less severe health declines than the other two species in response to oil and oil/dispersant mixture treatments, likely related to its increased abundance near natural hydrocarbon seeps. These experiments provide direct evidence for the toxicity of both oil and dispersant on deep-water corals, which should be taken into consideration in the development of strategies for intervention in future oil spills.

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Keywords: Deepwater Horizon, Deep sea, Oil spill, Dispersant, Corexit, Survival, Toxicity tests, Gulf of Mexico, gorgonian, octocoral, black coral, antipatharian

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1. Introduction

The *Deepwater Horizon* (DWH) oil spill was one of the largest environmental disasters in history, releasing approximately 5 million barrels of crude oil at depth in the Gulf of Mexico (GoM) over a three-month period (Crone & Tolstoy, 2010; Camilli *et al.*, 2011). In addition, nearly 7 million liters of oil dispersants were applied during the ensuing cleanup efforts. Dispersants are chemical emulsifiers that act to increase the rate of oil dispersion thereby increasing the amount of small oil droplets suspended in the water column, reducing oil slicks at the surface. Thus, dispersant applications affect the fate, transport and physical composition of oil. Of the 7 million liters of oil dispersants used, approximately 3 million liters were applied at depth for the first time in history (Barron, 2012), without a comprehensive understanding of how this subsea application might alter the fate of oil and impact benthic ecosystems (National Research Council, 2005).

Petroleum hydrocarbons released under high-pressure undergo a series of interconnected physical and chemical processes that affect their fate and transport in the deep sea (Camilli *et al.,* 2010; Kessler *et al.*, 2011; Reddy *et al.,* 2012). Following the direct injection of disperant (Corexit 9527A and 9500A) to the Macondo well head at a depth of 1544 meters (Hazen *et al.,* 2010), a large oil plume persisted for months centered at approximately 1100 meters (m) depth, without substantial biodegradation (Camilli *et al.*, 2010). Oil spewing from the wellhead encountered turbulent mixing and was emulsified as a result of its reduced buoyancy at depth and the application of dispersant (Fodrie & Heck Jr., 2011). Measurements of water-column samples collected from this

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deep-water plume (defined by Camilli *et al.*, 2010) indicated that a significant portion of water-soluble hydrocarbon components were retained in deep waters, with unknown portions of insoluble hydrocarbons drifting to the sea floor (Reddy *et al.*, 2012). Despite some emulsification of oil throughout the water column, surface waters were still polluted with oil slicks (Fodrie & Heck Jr., 2011). At the surface, some components of the oil were then transformed into aggregations of marine snow (and floc) by coagulation with suspended particulates and planktonic organisms. Although this marine snow disappeared from the surface layers of the GoM within a month, it is likely that it sunk into the deep sea as the oil weathered (Passow *et al.*, 2012).

Recent studies have found both lethal and sub-lethal effects of the DWH blowout on species inhabiting pelagic and coastal environments (Barron, 2012; Silliman *et al.*, 2012; Whitehead *et al.*, 2012; Dubansky *et al.*, 2013; Almeda *et al.*, 2013). Prior studies have shown variable levels of crude oil toxicity on aquatic organisms with some fauna being more susceptible than others (Anderson *et al.*, 1974; Bonsdorff *et al.*, 1990; Coull and Chandler, 1992; Stark *et al.*, 2003). Dispersant addition to the oil triggers a transient increase in hydrocarbon concentrations throughout the water-column (Pace *et al.*, 1995), which can then lead to higher, more toxic exposures of dissolved and dispersed oil components upon contact with marine life.

Spill-impacted deep-sea coral communities were first discovered at a depth of approximately 1370 m, 11 km southwest of the Macondo well explosion, at the lease block site Mississippi Canyon (MC) 294 (White *et al.* 2012). Various species of coral, primarily *Paramuricea biscaya* (Grasshoff, 1977), were found covered with brown flocculent material (floc), exhibiting characteristic signs of stress and mortality, including

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excess mucus production, sclerite enlargement, and tissue loss. Further analysis of this floc revealed hydrocarbons from the Macondo well were indeed present (White *et al.*, 2012). Whether the damage observed to the corals was induced by sinking oil-filled particulates, dissolved hydrocarbons, dispersants, or a combination of all of these sources is unknown. Subsequently, two additional sites were discovered to contain impacted deep-sea coral communities (Fisher *et al.* 2014).

Deep-sea corals alter the terrain of the sea floor and produce complex, heterogeneous habitat, which promotes benthic biodiversity (Cordes *et al.*, 2008, 2010). In addition to reef-forming scleractinian corals, which generally occur at upper-slope depths (300-1000 m), octocorals and black corals (antipatharians) form large, tree-like structures from the subtidal to over 3000 m depth. These corals colonize hard substrata, and can form dense fields (Roberts *et al.*, 2006). By increasing the complexity of the seafloor, they provide shelter, feeding areas, and nursery grounds for many fish and invertebrates.

Because deep-sea corals build the foundation for these communities, damage to them can impact biodiversity and ecosystem function (Husebo *et al.*, 2002, Freiwald *et al.*, 2004). Their longevity and slow growth rates make them particularly vulnerable to anthropogenic disturbance (Grigg, 1974; Emiliani *et al.*, 1978; Druffel *et al.*, 1990, 1995; Risk *et al.,* 1998, 2002; Andrews *et al.*, 2002; Adkins *et al.*, 2004; Roark *et al.*, 2009). As crude oil reserves are abundant in the GoM, with 1.5 billion barrels of oil extracted from the sea floor each day (Minerals Management Service, 2009), it is now a critical time for further examination of deep-sea coral response to oil and dispersant exposure.

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Here, the effects of oil, dispersant and oil-dispersant mixtures were tested experimentally on three species of deep-sea coral living near the DWH oil spill site in the Gulf of Mexico, including *Paramuricea* type B3 (Doughty *et al.,* 2014), *Callogorgia delta* (Bayer *et al.,* 2014) and *Leiopathes glaberrima* (as re-described in Opresko and Baron-Szabo 2001). *P. biscaya* was the most common of the corals impacted by the DWH oil spill (White *et al.*, 2012; Fisher *et al.* 2014), and *Paramuricea* type B3 is the sister species to this coral (Doughty *et al.*, 2014). *Paramuricea* type B3 was chosen because its shallower depth distribution (830-1090 m for *Paramuricea* type B3 vs. 1370-2600 m for *P. biscaya* with one individual collected at 850 m, Doughty *et al.* 2014) results in higher survivorship shipboard, and to avoid further impact to the relatively small populations of *P. biscaya* that have thus far been discovered. *C. delta* preferentially occupies habitats near natural oil seeps in the deep GoM (Quattrini *et al.*, 2013), suggesting that the species may have evolved a tolerance for hydrocarbon exposure. *L. glaberrima* is slow growing and lives to very old ages, making it one of the oldest skeletal secreting organisms known to date (Roark *et al.*, 2009). Slow growth rates make this species highly sensitive to natural and anthropogenic disturbances.

This study examined the effects of exposure to bulk oil-water mixtures, water-accommodated oil fractions (WAF), dispersants, and mixtures of hydrocarbons and dispersants using short-term toxicological assays (≤ 96hrs) that monitored phenotypic responses and survivorship. Specifically, we tested the hypotheses that oil/dispersant mixtures would be the most toxic to corals, and that *C. delta* would have a higher tolerance for hydrocarbons due to its affinity for natural seep habitats.

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2. Methodology

2.1 Sample collection and acclimatization

All samples were collected from two sites in the GoM. *C. delta* and *L. glaberrima* were collected from the Viosca Knoll 826 site at a depth of approximately 500 m (29°09.5'N, 88°01.0'W; Cordes *et al.,* 2008; Davies *et al.*, 2010). *Paramuricea* type B3 colonies were collected from a large population of corals at approximately 1050 m depth at Atwater Valley (AT) 357 (27°58.6'N, 89°70.4'W; Doughty *et al.* 2013). At each site, corals were haphazardly collected with the remotely operated vehicles (ROV) Global Explorer MK3 or Hercules.

Samples were taken on multiple dives, with 5-6 colonies of both *C. delta* and *L. glaberrima* collected from VK826, and 5-6 colonies of *Paramuricea* type B3 gathered from AT357. Samples were collected several meters apart from conspecific colonies to reduce the likelihood of sampling clones. Corals were visually identified using live video stream from cameras attached to each ROV, before being collected with a manipulator arm and secured in an insulated "bio" box and or sealable collection quivers. When possible, branches of colonies were sampled to reduce impact.

At the surface, colonies were immediately transferred to containers with filtered seawater of the species-appropriate temperature and salinity (35 psu). *C. delta* and *L. glaberrima* were jointly maintained at approximately 8°C and later, *Paramuricea* type B3 at 5°C (the average *in situ* temperatures at depth) in a temperature-controlled room for the duration of the experiment. Temperature in holding vessels was continuously monitored

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using temperature probes (Hobo® Data Loggers). Corals were allowed to acclimate for 6-12 hours prior to experimentation.

2.3 Preparation of bulk-oil treatments

For the bulk-oil experiment three stock solutions were prepared: crude oil (MASS oil collected from the Macondo well during the spill), dispersant (Corexit 9500A), an oil/dispersant mixture, and artificial seawater controls. All solutions were made with sterile artificial seawater (ASW, Instant Ocean™) at 35 psu, the average *in situ* salinity for both sites. ASW allowed us to accurately maintain desired salinity and temperature for large volumes of water without the potential for introducing contaminants from the ship's seawater system, and to avoid the unreliability of collecting buckets of seawater from over the side in variable sea states. We have used ASW to maintain other cold-water coral species alive in laboratory aquaria for extended periods of time without adverse affects (Lunden *et al.,* 2014).

A stock bulk-oil solution was prepared at a concentration of 250 parts per million (ppm) by adding 50 µL of MASS oil to 199.95 mL ASW. The solution was mixed at room temperature for a 24-hour period on an orbital shaker at approximately 500 rpm to achieve highest possible homogeneity. Oil dilutions were prepared from this stock solution. The subsequent oil concentrations were chosen in an attempt to determine the threshold for lethal toxicity, following preliminary toxicity studies on *L. glaberrima.* Dispersant concentrations were the same as the oil concentrations so as to examine the relative toxicity of oil vs. dispersant. The oil/dispersant-mixture stock solution was

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prepared with an initial targeted concentration of 250 ppm each of crude oil and Corexit 9500A by adding 50 μL of each to 199.90 mL of ASW. The dispersant stock solution was prepared by adding 50 μL Corexit 9500A to 199.95 mL ASW to achieve an initial concentration of 250 ppm. Serial dilutions were prepared from each of the three stock solutions to produce three target concentrations: 25 ppm (High), 7.9 ppm (Medium) and 0.8 ppm (Low).

All solutions were placed into sterile 50 mL glass vials. These were then incubated at 5 or 8 °C, dependent on species, and mixed continuously at low speeds for 24 hours on an orbital shaker table to reduce separation and to encourage even oil distribution. Experiments were conducted between the 8-27 November 2012 onboard the R/V Falkor.

2.4 Preparation of treatments using water-accommodated oil fractions (WAF)

For this experiment, stock solutions were prepared using only the water-accommodated oil fractions (WAF). For the WAF oil treatment, a higher oil volume (9.5 mL) of surrogate oil was added to 475 mL of ASW and mixed at high speeds (~350 rpm) in an attempt to produce a 1.2 mM WAF oil solution. The WAF was separated from the insoluble oil layer using a sterile separatory funnel, and used as a stock solution to produce experimental treatments with targeted initial total hydrocarbon concentrations of 250 μM (High), 150 μM (Medium) and 50 μM (Low) WAF. Target concentrations were chosen to find lethal doses, as none of the previous bulk-oil (only) concentrations proved to be lethal. This was done using a standardized WAF protocol (S. Joye, pers. com) and

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based on the highest concentrations of oil detected during the spill (~300 μM, Joye *et al.,* 2011).

The oil/dispersant mixture treatment was prepared using the same oil volume, with 950 μL of Corexit 9500A added (one-tenth of the oil concentration) to produce a dispersant enhanced WAF (DE-WAF; oil/dispersant treatment), also mixed at high speeds (~350 rpm). As the dispersant concentrations in the bulk-oil exposures were not entirely lethal to *C. delta* in the short term and most of the observed health decline was seen towards the end of the exposures at the highest Corexit 9500A concentration, the range of dispersant concentrations was progressively increased from those used in the previous exposures to attempt to reveal the lethal concentration (LC50). The dispersant stock solution was made by adding 950 μL of Corexit 9500A to 475 mL of ASW, with an initial dispersant concentration of 848 mg/L (mixed at 200-300 rpm). All stock solutions were mixed at room temperature for 48-72 hours. Experimental solutions were then made from these two treatments with targeted initial oil concentrations of 250 μM (High), 150 μM (Medium) and 50 μM (Low) and targeted initial total dispersant concentrations of 176.7 mg/L (High), 106.0 mg/L (Medium) and 35.3 mg/L (Low).

All solutions were placed into sterile 50 mL acid-washed glass vials prior to experimentation. There was an anticipated and unavoidable loss of hydrocarbons and dispersant due to the adhesion of hydrophobic components to the dilution containers with each sequential transfer, as well as the chemical and coral-microbial alterations of hydrocarbons and dispersant components over the course of the treatments. Therefore oil and dispersant concentrations are reported as conservative, initial targeted values only, and qualitatively designated as “High” “Medium” and “Low” in the analysis.

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Experiments were conducted from 23 June 2013 to 3 July 2013 onboard the R/V Nautilus.

2.5 Fragmentation and exposure experiments

For both bulk-oil and WAF experiments, four to six colonies of each species (n = 3) were fragmented into similar sized (approximately 3 cm to 6 cm tall), genetically identical replicates, or "nubbins" (n = 11) and placed into the oil, dispersant, oil/dispersant mixture and the control (ASW) treatments. *Paramuricea* type B3 had only three healthy colonies for the bulk-oil exposures. The number of polyps per nubbin varied for each species because of the wide range in polyp sizes and unique branching morphology. Samples were placed in 50 ml pyrex test tubes, mounted on a shaker table in a temperature controlled environment, and aerated every 24 hours by bubbling air into the tubes and gently inverting each sample.

Each sample was photographed together with a scale and monitored for signs of stress at four time points (24, 48, 72 and 96 hours) during the bioassay. Each experimental nubbin was assigned an overall health rating on a scale ranging from 0-5. The percentage of live polyps and tissue-covered skeleton primarily contributed to this rating: dead fragment (score of 0), <<50 percent (score of 1-2), ~50 percent (score of 3), >>50 percent (score of 4-5), while the other stress responses further differentiated between scores. Ratings were further refined based on the following phenotypic stress responses: percentage of polyp retraction and or inflation, presence and persistence of mucus discharge, dead or darkened tissue, sloughing tissue and exposed skeleton. While polyp mortality, polyp retraction, mucus release, loose tissue, and exposed skeleton were

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observed in all three species, swollen polyps were only observed in *L. glaberrima*, while darkened tissue was specific to *Paramuricea*. Tissue discoloration and whitening was only observed in *C. delta*. Furthermore, *C. delta* displayed a distinctive polyp coiling, ultimately forming node-like structures that eventually disintegrated, leaving behind exposed skeleton. Samples and treatments were randomized in an attempt to reduce health-scoring bias.

2.6 Survival Analysis

Health rankings were averaged for replicate coral fragments in each experimental concentration and plotted over time to investigate health decline. This was done discretely for each round of experiments (bulk-oil or WAF), type of treatment (oil, dispersant and oil/dispersant) and species to determine the effect of concentration on fragment health over time. Health differences within the different treatments at the 96-hour end-point were tested using a non-parametric Kruskal-Wallis test, and if applicable ($p < 0.05$), non-parametric post-hoc, pair-wise comparisons were performed using the Wilcoxon method (using JMP® Pro 10.0.2).

To investigate fragment survival over time, a Kaplan-Meier (K-M) "time to event" survival analysis was performed separately for each experimental series (IBM® SPSS® Statistics v22, Kaplan & Meier, 1958). This test measures the fraction of fragments declining to a health status of 3 or below at each time point and generates a survival curve. To quantify differences amongst the survival curves for a given species and treatment, a Mantel-Cox Log-rank test was used to evaluate statistical significance (

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= 0.05); if significant, pair-wise comparisons were made, again using a Mantel-Cox Log-rank test.

An additional K-M analysis was performed to compare survival across species in each treatment. Only "event" occurrences contribute to survival estimates; the remaining data becomes censored in the analysis. For this reason the ASW control treatments, in which all fragments maintained health ratings > 3, were excluded from survival-estimate statistics during species comparisons. A similar percentage of censored cases were present in the oil, dispersant and oil-dispersant treatments for each species, and the pattern of censoring was similar.

Additionally, Cox regressions were performed to quantify the hazard (i.e. a decline in health) associated with a) treatment (Water, Oil, Dispersant/Oil and Dispersant), b) concentration (High, Medium, Low, Zero), and c) species (*C. delta*, *L. glaberrima*, *Paramuricea* type B3) for the two sets of experiments (bulk-oil and WAF). The "event" in the time-to-event analysis was reaching a health rating of 3 or below (3, 1, 2 or 0), as mortality was not observed in every treatment and concentration during the exposure. The hazard ratios were calculated for each factor with respect to control treatment (a), the zero concentration (b) and *C. delta* (c), as we had hypothesized this to be the species most likely adapted to oil exposure. Cox regression was performed in IBM® SPSS® Statistics v22.

3. Results

3.1 Exposure effects on *Paramuricea* type B3

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3.1.1 Oil treatment

Complete fragment mortality was not observed for *Paramuricea* type B3 in the control, bulk-oil or oil-WAF treatments (Figure 1, A; Figure 2, A). In examining the effect of concentration on fragment condition at the end of the bulk-oil and WAF exposures, the Kruskal-Wallis test showed no significant differences among the 96-hour health ratings across all oil concentrations and controls ($p > 0.05$).

3.1.2 Dispersant treatment

Whole fragment mortality was observed in *Paramuricea* type B3 nubbins exposed to the High dispersant treatment (Figure 1, D). This decline in health originated in the dispersant mixture within 48-72 hours, with two of three colonies exhibiting complete fragment mortality at the end of the exposure period. The Kruskal-Wallis test revealed significant differences ($p < 0.05$) in health rankings for *Paramuricea* type B3 at the end of the exposure; pair-wise comparisons revealed significant differences between nubbins in the High dispersant relative to the control samples ($p < 0.05$).

High coral fragment mortality was observed in the dispersant treatment across all concentrations tested in the WAF experiments. One of six *Paramuricea* type B3 replicates died in the Low dispersant solution, with complete mortality observed in four of six replicates in the Medium dispersant treatment by 96 hours. At High dispersant concentrations, four of six replicates were dead after only 48 hours, with complete mortality of all fragments after 96 hours (Figure 2, D). The Kruskal-Wallis test and pair-wise comparisons revealed significantly higher health ratings among the control

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Paramuricea type B3 nubbins relative to all levels of dispersant (Low, Medium and High; $p < 0.005$) as well as in the Low versus High dispersant concentrations ($p < 0.005$).

3.1.3 Oil/dispersant treatment

Whole fragment mortality was observed in *Paramuricea* type B3 nubbins exposed to the High oil/dispersant treatment (Figure 1, G), with complete mortality in two of three fragments by 96 hours. There were significant health differences among concentrations (Kruskal-Wallis, $p < 0.05$), and subsequent pair-wise comparisons revealed significant differences between fragments in the High oil/dispersant relative to the control samples ($p < 0.05$).

During the WAF exposures, complete mortality was observed in the oil/dispersant mixture (DE-WAF), for one of six *Paramuricea* type B3 samples in both the Low and High concentrations (Figure 2, G). The Kruskal-Wallis and post-hoc tests detected significant health differences in fragments exposed to all concentrations of the mixture relative to the controls ($p < 0.05$).

3.1.4 Comparisons between treatments for *Paramuricea* type B3

For comparisons made between treatments in the bulk-exposure series, the log-rank test revealed significant differences among the K-M survival estimates (┘ = 7.62, df = 2, $p = 0.022$); pairwise comparisons (Table 1) indicated these differences were between the oil and oil/dispersant treatments ($p < 0.0167$). The oil/dispersant treatment had the lowest mean estimated survival time of 87.6 hrs, compared to the overall mean estimate of 90.2 hrs (Table 2a, Figure 3). In the WAF exposures there were also significant

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differences among time-to-event occurrences ($^{\lrcorner}$ = 57.3, df = 2, $p < 0.001$), and pair-wise comparisons affirmed significantly different estimates between all treatments. The lowest time-to-event estimate was 82.5 hrs in dispersant compared to 96 hrs in oil and an overall average estimate of 90.8 hrs (Table 2b, Figure 3).

3.2 Exposure effects on *Callogorgia delta*

3.2.1 Oil treatment

There was no complete fragment mortality in the co ntrol or bulk-oil treatments (Figure 1, B). However, one *C. delta* replicate in the Low oil-WAF died by the end of the exposure (Figure 2, B). The Kruskal-Wallis test showed no significant differences among the 96-hour health ratings across all concentrations of bulk and WAF oil ($p > 0.05$).

3.2.2 Dispersant treatment

C. delta showed a decline in health in the High dispersant (Figure 1, E), though complete fragment mortality was not observed during the 96 hour assay. The Kruskal-Wallis test revealed significant differences ($p < 0.05$) in health rankings, with the High dispersant showing a significantly greater decline in health than the Medium and Low concentrations ($p < 0.05$).

During the WAF exposures, 75 percent of *C. delta* fragments died in the Low dispersant, 25% in the Medium and 75% in the High dispersant after 96 hours (Figure 2,

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E). Control fragment health was significantly higher relative to all concentrations of dispersant ($p < 0.05$).

3.2.3 Oil/dispersant treatment

Coral fragments also showed a decline in health within the High oil/dispersant treatment (Figure 1, H), but again complete fragment mortality was not observed. Significant differences were detected between nubbins in the High oil/dispersant relative to the control samples ($p < 0.05$).

During the DE-WAF exposures, mortality was observed in one colony in the Medium concentration and three of the four colonies in the High concentration (Figure 2, H). A Kruskal-Wallis test revealed significant health differences among treatments, with the Medium and High DE-WAF treatments significantly lower than the controls ($p < 0.05$), and the High DE-WAF also significantly lower than the Low treatment ($p < 0.05$).

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3.2.4 Comparisons between treatments for *C. delta*

No significant differences were detected among K-M time-to-event estimates for *C. delta* fragments in all treatments within the bulk-oil series ($\lrcorner = 1.72$, df = 2, $p = 0.422$), with an overall time-to-event (health rating of 3 or less) estimate of 91.4 hrs (Table 2a, Figure 3). However, significant differences were detected among treatment estimates in the WAF series ($\lrcorner = 12.5$, df = 2, $p = 0.002$); these differences were between the oil-only and dispersant-only treatments (Table 1). The lowest estimate was 89.1 hrs in the

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dispersant treatment relative to the 93.5 hrs in the oil, and an overall average time-to-event estimate of 91.6 hrs (Table 2b).

3.3 Exposure effects on *Leiopathes glaberrima*

3.3.1 Oil treatment

There was no complete fragment mortality for *L. glaberrima* nubbins in the control, bulk-oil (Figure 1, C) or oil-WAF treatments (Figure 2, C). However, the Kruskal-Wallis test detected significant differences ($p < 0.05$) among fragment health ratings in bulk-oil mixtures at 96 hrs; this difference was due to lower rankings in the Medium oil compared to those in the Low oil ($p < 0.05$) and the controls ($p = 0.01$), although rankings were similar between the Medium and High oil concentrations.

There was a significant difference among *L. glaberrima* health ratings in the oil-WAF exposure ($p < 0.001$); pairwise comparisons revealed that all concentrations of oil had significantly higher health ratings than control fragments ($p \leq 0.005$). Ratings in the Medium oil-WAF were also significantly higher than the Low and High ($p < 0.05$) oil concentrations.

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3.3.2 Dispersant treatment

Whole fragment mortality was not observed for *L. glaberrima* samples, though there was a decline in health within the High dispersant treatment (Figure 1, F). The Kruskal-Wallis test also detected no significant differences among sample health ratings at 96 hours ($p > 0.05$).

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During the WAF exposures, *L. glaberrima* samples in the High and Medium dispersant concentrations were dead by 72 hours. By 96 hrs four of six fragments were also dead in the Low dispersant treatment (Figure 2, F). The Kruskal-Wallis test revealed significantly lower health ratings in all concentrations of dispersant: Low ($p < 0.05$), Medium and High ($p < 0.005$) relative to controls.

3.3.3 Oil/dispersant treatment

Whole fragment mortality was not observed in the bulk-oil/dispersant mixture (Figure 1, I). The Kruskal-Wallis test and pair-wise comparisons revealed significant health differences between *L. glaberrima* samples in the High and Medium oil/dispersant ($p < 0.05$) and between both the High and Medium concentrations relative to the control samples ($p \leq 0.01$).

For *L. glaberrima* samples in the DE-WAF, there was complete sample mortality in the High concentration by 72 hrs, with two of six colonies dead in the Medium DE-WAF (Figure 2, I). Health ratings for nubbins in the control and Low DE-WAF were significantly higher than those in the Medium and High concentrations ($p < 0.005$).

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3.3.4 Comparisons between treatments for *L. glaberrima*

The K-M analysis and log rank test revealed significantly different time-to-event estimates for *L. glaberrima* samples ($^{\lrcorner}$ = 7.20, df = 2, p = 0.027). Pairwise comparisons (Table 1) indicated this difference was between both the oil and dispersant treatments

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relative to the oil/dispersant mixture, which had the shortest time-to-event estimate of 91.0 hrs compared to an overall time-to-event estimate of 94.0 hrs (Table 2a, Figure 3). Significant differences were also detected among time-to-event estimates in the WAF exposures (┘ = 61.7, df = 2, $p < 0.001$) across all treatments. The lowest time-to-event estimate was in the dispersant treatment (77.8 hrs) with the highest estimate (96 hrs) in the oil treatment and an overall estimate of 86.4 hrs (Table 2b, Figure 3).

3.4 Overall comparisons between treatments and concentrations

The Cox regression analysis for the bulk-oil series revealed significant differences (┘ = 57.8, df = 5, $p < 0.001$) among rates in health decline (to health-rating 3, ~50% survival) among treatments (control, oil, dispersant and oil/dispersant) and concentrations (zero, low, medium and high). The High concentration significantly increased the hazard of reaching a health rating of 3 or below by 2.5 fold relative to control concentrations, but the Medium concentration did not significantly increase the hazard. Also, relative to controls, samples in the dispersant had an increased hazard risk of 2.3 fold, however the hazard increase in the bulk-oil and oil/dispersant mixture treatments were not significantly different from the control treatment.

Similar regression analyses for the WAF exposures also revealed significant differences (┘ = 176.470, df = 7, $p < 0.001$) among rates of health decline between treatments and concentrations. Relative to the controls, dispersant significantly increased the hazard of reaching a health rating of 3 or below by 3.4 fold, compared to 4.4 fold in the oil/dispersant treatment; being exposed to oil did not significantly increase the hazard. In addition, the medium treatment concentrations significantly increased the hazard by

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1.3 fold relative to the control concentration, whereas the high concentration increased it by 1.6 fold (Table 4).

3.5 Comparisons between species

Significant differences between K-M survival estim ates were detected within the dispersant treatment as well as the control treatment during species comparisons for the bulk-oil series ($p < 0.05$; Table 5). The lowest time-to-event estimate of 90.3 hrs was for *Paramuricea* type B3 compared to an overall time-to-event estimate of 94.4 hrs. However, adding species into the Cox regression model did not improve fit, as species' rate of decline comparisons were not significantly different.

In the WAF exposures, these differences ($p < 0.001$) were also detected among species in the oil and oil/dispersant treatments. The lowest time-to-event estimate in oil was for *Paramuricea* type B3 at 68.8 hrs relative to 75.9 hrs for *L. glaberrima*, 85.2 hrs for *C. delta* and an overall time-to-event estimate of 76.3 hrs. *Paramuricea* type B3 (64.3 hrs) and *L. glaberrima* (65.3 hrs) had similarly low time-to-event estimates in the oil/dispersant treatment relative to 93.5 hrs for *C. delta* and an overall time-to-event estimate of 73.1 hrs. The Cox regression model also indicated that overall, *L. glaberrima* did significantly worse than *C. delta* by 1.3 fold but decline rates for *Paramuricea* type B3 were not significantly different from those of *C. delta* (Table 4).

4. Discussion

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All three deep-sea coral species examined showed more severe declines in health in response to dispersant alone and the oil-dispersant mixtures than the oil-only treatments. The experiments reported here are the first ever to investigate the effects of oil and dispersant exposure on live, cold-water corals collected from the deep sea. Impacted corals have been observed at multiple sites in the deep GoM (Fisher *et al.* 2014), some covered with floc linked to oil from the Macondo well explosion (White *et al.*, 2012). However, the unprecedented application of chemical dispersants in the deep-sea may have contributed to the observed pattern of impact. This exposure series provides crucial insight into the toxicological impacts of oil and dispersant release on three species of long-lived, habitat forming corals.

Regarding the components of the bulk-oil and WAF mixtures, hydrocarbon concentrations are likely an overestimate, given crude oil's variable and complex composition, containing thousands of compounds differing in hydrophobic and hydrophyllic tendencies (Clark Jr. & Brown, 1977; Singer *et al.,* 2000; Di Toro *et al.*, 2007). Dispersants also contain a variety of polar and non-polar surfactants and solvents (Singer *et al.*, 1996). It is highly probable that there was adhesion of oil and dispersant constituents to the mixing flasks used during serial dilutions, as well as to experimental vials. Moreover, loss of water-accomodated oil fractions may have occurred through coalescence and surfacing throughout the exposure period (particularly in the bulk-oil exposure), volatilization during aeration, and/or biodegradation from the microbial communities associated with coral tissues (Couillard *et al.*, 2005). Thus, it is difficult to determine the precise concentrations of oil and dispersant that each coral fragment may encounter at any given time during the course of the experiment but clearly actual

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exposures were lower than target values, making our results conservative estimates of the effects of oil, dispersant and oil/dispersant mixtures on deep-sea corals. Indeed, similar trends in health decline were observed within each treatment for all three species during four separate experimental trials.

The goal of this experiment was not to reproduce t he exact conditions encountered by deep-water corals during the DWH spill, but rather to provide experimental evidence of their sensitivity to various concentrations of oil and dispersant. Reproducing exact conditions encountered by deep-water corals during the DWH spill is challenging because oil, dispersant and seawater mixtures form complex multiphase systems; an organism may then be exposed to many components of the oil and dispersant in various forms (National Research Council, 1989; Langevin *et al.*, 2004). It is also important to note that corals within the vicinity of the DWH may have been exposed to these pollutants for longer than 96 hours. Long-term exposures may see additional effects but were not feasible due to the time limitations of experimenting at sea. There is also a low survival rate when transporting deep-sea corals back to laboratory aquaria; *C. delta and L. glaberrima* only survive for approximately 1-3 months, whereas we have had no success keeping *Paramuricea* type B3 or *P. biscaya* alive over the long-term.

All three species of corals did surprisingly well in the oil treatments compared to the dispersant and oil/dispersant treatments (Figures 1 & 2). In some cases, the corals appeared healthier in both the bulk-oil and oil-WAF treatments relative to the controls (e.g. *C. delta* and *L. glaberrima*, Figures 1 & 2). Although corals can be negatively impacted when covered by oil particulates or floc (White *et al.*, 2012), it is also possible that corals are deriving some form of nutrition from hydrocarbon components, a process

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that is likely to be mediated by their associated microbial communities. Anecdotal evidence for this linkage comes from the finding of at least one species of octocoral (*Callogorgia delta*) with increased abundances around natural hydrocarbon seeps (Quattrini *et al.*, 2013). Previous studies of shallow-water octocorals also revealed non-selective hydrocarbon uptake of dispersed oil droplets into the gastrovascular cavity of the coral during water uptake (Cohen *et al.*, 1977). Since additional food sources were not supplied during the exposure experiments, and most coral fragments within the oil treatments were frequently observed with a higher degree of polyp extension, similar uptake of dispersed oil components might have occurred.

Although our present study suggests MASS crude oil was not toxic over the range of concentrations tested in these experiments (Figures 1 & 2), the effect of oil exposure on corals may be dependent on life-history stage. Crude oil (from the Macondo well) exposures of scleratinian coral larvae induced mortality within 24 hours, while reducing settlement capabilities and post-settlement survival (Goodbody-Gringley *et al.*, 2013). This suggests an increased vulnerability for coral planulae larvae and juvenile stages, although there was an influence of larval size on exposure tolerance. Other studies have shown premature ejection of planula larvae after exposure to water-soluble fractions of Iranian crude oil (Loya & Rinkevich, 1979) and sub-lethal oil damage to the female reproductive systems of scleratinian corals (Rinkevich & Loya, 1979). Similar sub-lethal impacts may have been imposed on cold-water corals exposed to oil released from the DWH disaster, although these effects may not be manifested for a number of years.

Treatments containing dispersants in both exposure experiments were the most toxic to the corals and induced the highest degree of overall fragment mortality (Figures 1

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& 2). As dispersants tend to increase the surface area of oil-water interactions, they may cause increased toxicological effects to marine organisms (Chandrasekar *et al.*, 2006; Goodbody-Gringley *et al.*, 2013). However, in the WAF exposure series, dispersant-only solutions were more lethal than the oil/dispersant mixture treatments (as compared to the bulk-oil exposure series), though both treatments resulted in some mortality (Figures 1 & 2). Toxicity of dispersants is typically attributed to membrane disruption and impairment via surface-active compounds (Abel, 1974; National Research Council, 1989). Exposure results in increased permeability of biological membranes, loss of total membrane function and/or osmoregulation (Benoit *et al.,* 1987; Partearroyo *et al.,* 1990). Although Corexit 9500A was created in an attempt to reduce the toxicity of its predecessors while increasing effectiveness for dispersing more vicous oils, studies have shown that exposure effects are similar to older formulations, Corexit 9527 and 9554 (Singer *et al.*, 1991, 1995, 1996), which are now considered toxic to a variety of marine organisms.

The results from this toxicological assay suggest that dispersant addition during the ensuing cleanup efforts following the DWH spill may have caused more damage to cold-water corals than the initial release of crude oil into the deep sea. Dispersants were toxic at the higher concentrations tested here, and dispersed oil solutions proved to be more toxic than untreated oil solutions (Figure 1 & 2), as has been found in previous studies (Epstein *et al.*, 2000; Mitchell and Holdway, 2000; Shafir *et al.*, 2003; Bhattacharyya *et al.*, 2003; Milinkovitch *et al.*, 2011; Rico-Martinez *et al.*, 2013). The ability of different types of dispersants to emulsify petroleum hydrocarbon components into the water column as well as the relative toxicity of the dispersants and crude oil, contribute to the overall toxicity of each solution (Epstein *et al.*, 2000). The dispersant

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and oil/dispersant treatments were lethal to all three species in this study, particularly in the WAF exposure series where dispersant concentrations were higher.

It has been observed in several toxicology studies that dispersant additon increases the total concentration of polycyclic aromatic hydrocarbon (PAH) components in surrounding water (Couillard *et al.*, 2005; Hodson *et al.*, 2007). Specifically, it increases the concentration of less water-soluble high-molecular-weight PAHs, some of which induce enzymatic activity (i.e. cytochrome P4501A) that can metabolize PAHs into toxic forms causing a variety of detrimental effects (Henry *et al.*, 1997; Billiard *et al.*, 1999; Couillard *et al.*, 2005). This could explain the more rapid decline in health for coral fragments exposed to the bulk-oil/dispersant and oil-WAF/dispersant mixtures, where it was likely that a larger proportion of crude oil compounds were made biologically available (Couillard *et al.*, 2005; Schein *et al.*, 2009). Larval exposure experiments on two species of shallow-water scleractinian corals, using BP Horizon source oil and Corexit 9500A, showed a significant decrease in survival and settlement in dispersant solutions and oil-dispersant mixtures, with complete mortality after exposure to 50-100 ppm solutions of dispersant (Goodbody-Gringley *et al.*, 2013). In larvae of hard and soft coral species exposed to dispersants and Egyptian crude oil, all dispersant treatments were more toxic than the oil-only treatments with the highest toxicity observed in oil-dispersed solutions, which also resulted in abnormal development and tissue degeneration (Epstein *et al.,* 2000).

Despite these results, it is unclear whether short-term exposures to oil and dispersant have long-term effects. Following brief (~24 hours) exposures to Arabian crude oil or dispersed-oil (with Corexit 9527), there were no significant long-term effects

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on the yearly *in situ* skeletal growth of shallow water, hermatypic corals in the genus *Diploria* and *Acropora* (Dodge *et al.*, 1984; LeGore *et al.*, 1989). Though variability in growth rates during that year were not measured, similar experiments using a different scleractinian coral, *Porites furcata*, did reveal reduced growth in exposed fragments relative to controls (Birkeland *et al.*, 1976). This indicates that although short exposure to oil and dispersant may not be lethal to these corals, additional sub-lethal impacts are possible, the extent of which need to be investigated further.

Oil transport to benthic sediments likely occurred through a variety of pathways after the DWH spill, including direct particulate sinking and absorption into marine snow (Passow *et al.*, 2012). Exposure to oil-filled particulates may be more damaging to corals then the dissolved hydrocarbon components when additional stressors are present. As viscous particulates, such as flocs, settle onto benthic communities, the unavoidable exposure imposes many risks (Montagna *et al.*, 2013) including the suffocation of sessile organisms. Floc was likely trapped in the mucous of corals (White *et al.*, 2012) and may have also triggered the excretion of excess mucus in an attempt to remove the debris. This is an energetically costly mechanism, which may lead to reduced health when coupled to additional environmental stressors (Crossland *et al.*, 1980; Riegl & Branch, 1995).

In conclusion, exposure to relatively high concent rations of crude oil does not appear to be as lethal to these species of deep-sea corals as dispersant and mixtures of hydrocarbons and dispersant. However, it is possible that a longer exposure to sub-lethal oil concentrations may cause adverse effects that could not be observed in this short-term toxicological assay. Further examination into the relative effectiveness of different types

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of dispersants, coupled to examinations of their relative toxicity, is required. To improve future response efforts, alternative methods of oil cleanup are needed, and caution should be used when applying oil dispersants at depth, as it may induce further stress and damage to deep-sea ecosystems.

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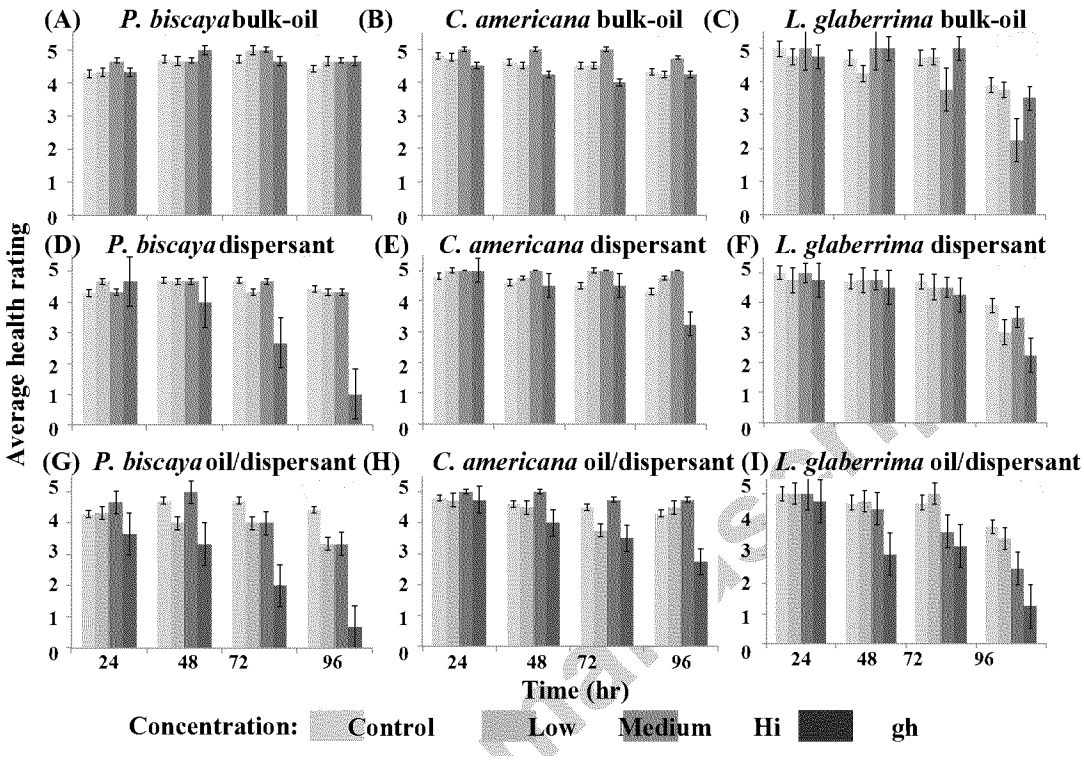

Figure 1- Average health ratings over time for coral fragments exposed to various concentrations of bulk-oil mixtures (yellow), Corexit 9500A dispersant solutions (blue) and oil-dispersant (oil/disp.) combination mixtures (red). Health rating scale 0-5. Bars show standard error.

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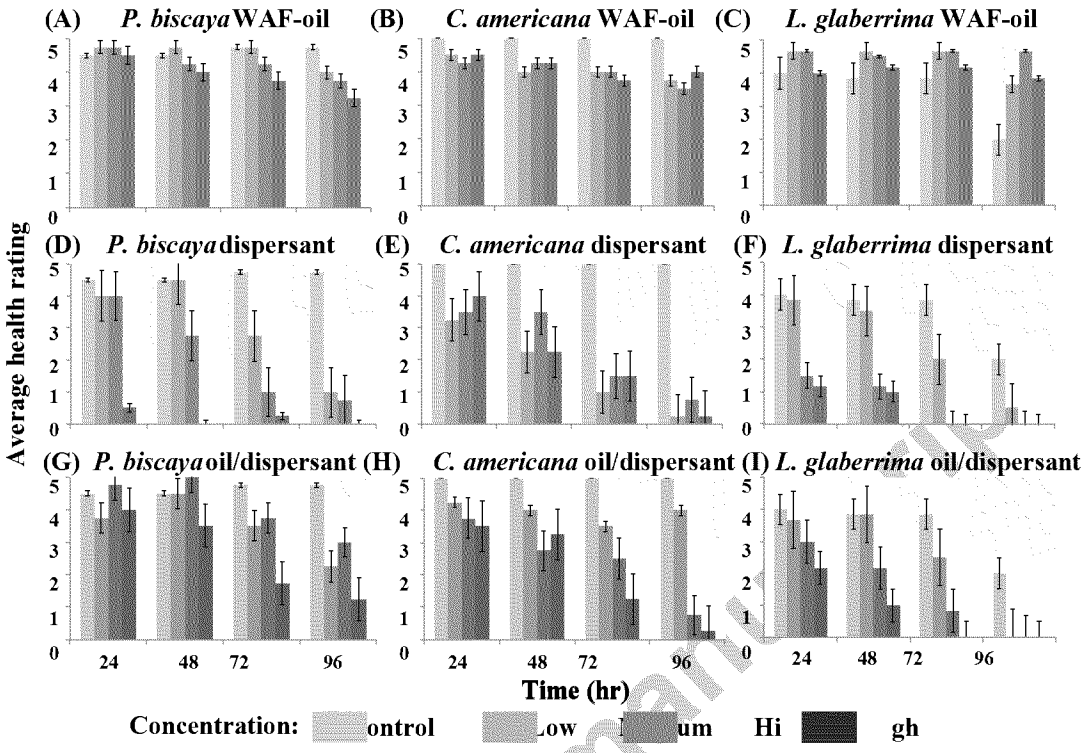

Figure 2- Average health ratings over time for coral fragments exposed to various concentrations of water accommodated oil fractions (yellow), Corexit 9500A dispersant solutions (blue) and water accommodated oil-dispersant (oil/disp.) combination mixtures (red). Health rating scale 0-5. Bars show standard error.

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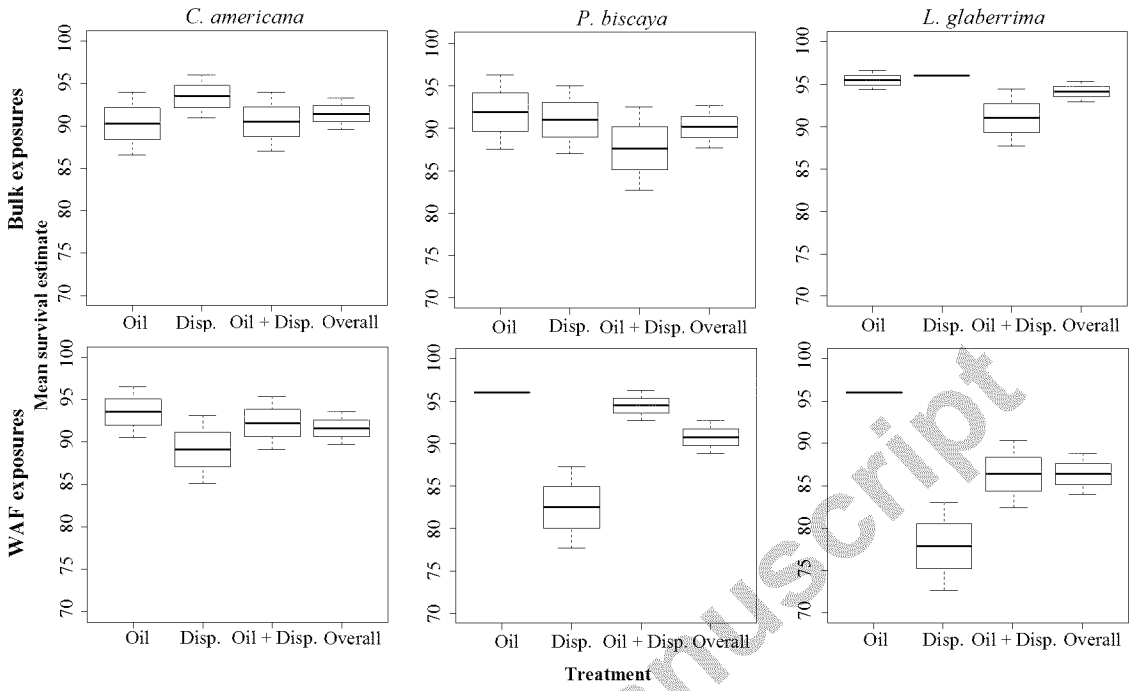

Figure 3- Box-plots showing time-to-event estimates from the Kaplan-Meier survival analysis for coral fragments in three different treatments: oil, dispersant and oil/dispersant (Top row represents bulk-oil exposures and bottom row represents oil WAF exposures). The event was a decline in health rating to 3 or below (bulk) and 1 or below (WAF). Box ends represent standard error, line inside the box represents the mean and whiskers represent 95% confidence intervals.

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Table 1- Pair-wise comparisons of K-M survival estimates in oil, dispersant and oil/dispersant treatments within the bulk-oil and oil-WAF exposure series, using a Mantel-Cox log-rank analysis. Comparisons were done discretely for each of the three coral species *C. delta, Paramuricea* (type) B3 and *L. glaberrima* (| ^{2}= chi-square, └= 0.05). The event was a decline in health rating to 3 or below (bulk) or 1 and below (WAF). Bonferroni adjusted p-values for each within species comparison are $p < 0.0167$.

Log-rank (Mantel-Cox)		**Oil**		**Dispersant**		**Oil /Dispersant**	
		^{2}	**p-val**	^{2}	**p-val**	^{2}	**p-val**
Bulk exposures	Oil	–	–	1.766	0.184	0.284	0.594
C. delta	Dispersant	1.766	0.184	–	–	3.594	0.058
	Oil/Dispersant	0.284	0.594	3.594	0.058	–	–
Paramuricea B3	Oil	–	–	3.958	0.047	10.634	**0.001**
	Dispersant	3.958	0.047	–	–	2.401	0.121
	Oil/Dispersant	10.634	**0.001**	2.401	0.121	–	–
L. glaberrima	Oil	–	–	0.152	0.696	7.364	**0.007**
	Dispersant	0.152	0.696	–	–	6.919	**0.009**
	Oil/Dispersant	7.364	**0.007**	6.919	**0.009**	–	–
WAF exposures	Oil	–	–	14.127	**0.000**	4.788	0.029
C. delta	Dispersant	14.127	**0.000**	–	–	3.651	0.056
	Oil/Dispersant	4.788	0.029	3.651	0.056	–	–
Paramuricea B3	Oil	–	–	46.594	**0.000**	8.695	**0.003**
	Dispersant	46.594	**0.000**	–	–	25.770	**0.000**
	Oil/Dispersant	8.695	**0.003**	25.770	**0.000**	–	–
L. glaberrima	Oil	–	–	65.367	**0.000**	45.871	**0.000**
	Dispersant	65.367	**0.000**	–	–	6.077	**0.014**
	Oil/Dispersant	45.871	**0.000**	6.077	**0.014**	–	–

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Table 2- K-M means for time-to-event estimates for three coral species: *C. delta, Paramuricea* type B3 and *L. glaberrima*, in bulk-oil (a) and WAF (b) exposures using a Mantel-Cox Log-rank analysis. The event was a decline in health rating to: a) 3 or below, b) 1 or below.

(a)Bulk exposure				95% Confidence Interval	
Species	Treatment	Survival Estimate	Std. Error	Lower Bound	Upper Bound
C. delta	Bulk-oil	90.3	1.88	86.6	94.0
	Dispersant	93.5	1.31	90.9	96.0
	Oil/Dispersant	90.5	1.77	87.1	94.0
	Overall	91.4	0.95	89.6	93.3
Paramuricea type B3	Bulk-oil	91.9	2.25	87.5	96.3
	Dispersant	91.0	2.04	87.0	95.0
	Oil/Dispersant	87.6	2.50	82.7	92.5
	Overall	90.2	1.27	87.7	92.7
L. glaberrima	Bulk-oil	95.4	0.57	94.3	96.6
	Dispersant	96.0	0.00	96.0	96.0
	Oil/Dispersant	91.0	1.71	87.7	94.4
	Overall	94.1	0.62	92.9	95.4
Overall	Overall	92.1	0.54	91.0	93.1

(b)WAF exposure				95% Confidence Interval	
Species	Treatment	Survival Estimate	Std. Error	Lower Bound	Upper Bound
C.delta	Oil WAF	93.5	1.52	90.5	96.5
	Dispersant	89.1	2.05	85.1	93.1
	Oil/Dispersant	92.3	1.60	89.1	95.4
	Overall	91.6	0.99	89.7	93.6
Paramuricea type B3	Oil WAF	96.0	0.00	96.0	96.0
	Dispersant	82.5	2.45	77.7	87.3
	Oil/Dispersant	94.5	0.88	92.8	96.2
	Overall	90.8	0.98	88.9	92.7

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L. glaberrima	Oil WAF	96.0	0.00	96.0	96.0
	Dispersant	77.8	2.63	72.7	83.0
	Oil/Dispersant	86.4	2.01	82.4	90.3
	Overall	86.4	1.23	84.0	88.8
Overall	Overall	89.3	0.64	88.1	90.6

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Table 3- Log-rank tests of equality on survival distributions for the different levels of concentration in the bulk-oil and WAF exposure series. Significant p-values ($p < 0.05$) in bold.

Overall log-rank comparisons among concentrations				
Bulk-oil series				
Treatment		Chi-Square	df	Sig.
Control	Log Rank (Mantel-Cox)	-	0	-
Bulk-oil	Log Rank (Mantel-Cox)	0.548	2	0.760
Dispersant	Log Rank (Mantel-Cox)	15.635	2	**0.000**
Oil/Dispersant	Log Rank (Mantel-Cox)	21.793	2	**0.000**
WAF-oil series				
Control	Log Rank (Mantel-Cox)	-	0	-
WAF-oil	Log Rank (Mantel-Cox)	1.190	2	0.552
Dispersant	Log Rank (Mantel-Cox)	33.246	2	**0.000**
Oil/Dispersant	Log Rank (Mantel-Cox)	20.061	2	**0.000**

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Table 4- Predictor variables in Cox regression analysis and calculated hazard ratios of the odds of reaching health-ratings of interest (≤ 3) for the Bulk-oil and WAF-oil exposure series. Significant differences based on Wald test statistics; Low concentration is not present because values are constant or linearly dependent. Hazard ratios were calculated relative to the control water treatment, 0 mg/L concentration and the species *C. delta,* respectively.

	Cox regression variables					
	Bulk-oil					
Variable	**Level**	**Wald**	**df**	**p**	**Hazard ratio**	**Standard error**
Treatment	Treatment	14.908	3	**0.002**	-	-
	Bulk-oil	0.011	1	0.918	0.963	0.355
	Dispersant	7.067	1	**0.008**	2.322	0.317
	Oil/disp.	0.123	1	0.725	1.133	0.367
Concentration	Concentration	19.279	2	**<0.001**	-	-
	Med conc.	0.272	1	0.602	0.833	0.350
	High conc.	10.795	1	**0.001**	2.500	0.279
Species	Species	0.745	2	0.689	-	-
	Paramuricea type B3	0.013	1	0.908	1.027	0.231
	L. glaberrima	0.645	1	0.422	1.212	0.239
	WAF-oil					
Treatment	Treatment	95.263	3	**<0.001**	-	-
	WAF-oil	0.026	1	0.872	0.957	0.276
	Dispersant	27.407	1	**<0.001**	3.404	0.234
	Oil/disp.	41.745	1	**<0.001**	4.417	0.230
Concentration	Concentration	10.977	2	**0.004**	-	-
	Med conc.	3.912	1	**0.048**	1.342	0.149
	High conc.	10.977	1	**0.001**	1.608	0.143
Species	Species	15.701	2	**<0.001**	-	-
	Paramuricea type B3	1.807	1	0.179	0.817	0.137
	L. glaberrima	4.617	1	**0.032**	1.342	0.151

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Table 5- Log-rank tests on equality of survival distributions for all species in the bulk-oil and WAF exposure series. Significant p-values ($p < 0.05$) in bold.

Overall log-rank comparisons among species				
Bulk-oil series				
Treatment		**Chi-Square**	**df**	**p-value**
Control	Log Rank (Mantel-Cox)	11.222	2	**0.004**
Bulk-oil	Log Rank (Mantel-Cox)	2.496	2	0.287
Dispersant	Log Rank (Mantel-Cox)	6.622	2	**0.036**
Oil/Dispersant	Log Rank (Mantel-Cox)	5.709	2	0.058
WAF-oil series				
Control	Log Rank (Mantel-Cox)	60.353	2	**<0.001**
WAF-oil	Log Rank (Mantel-Cox)	7.556	2	0.023
Dispersant	Log Rank (Mantel-Cox)	2.584	2	0.275
Oil/Dispersant	Log Rank (Mantel-Cox)	22.22	2	**<0.001**

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Biodegradability and toxicity of sulphonate-based surfactants in aerobic and anaerobic aquatic environments

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Aquatic toxicity

abstract

Four types of commonly used sulphonate-based surfactants (alkane sulphonates, alpha-olefin sulphonates, sulphosuccinates and methyl ester sulphonates) were tested for their aerobic and anaerobic biodegradability as well as for their toxicity to Daphnia magna and Photobacterium phosphoreum to assess the effect of the surfactant structure on those properties. Aerobic biodegradation was evaluated by means of the CO_2 headspace test and anaerobic biodegradation was assessed by a method based on the ECETOC test. [redacted] No clear effect of the surfactant structures on the toxicity to the aquatic organisms tested was found. The most significant differences in the surfactants studied were observed in their behaviour under anaerobic conditions. Alkane sulphonates, alpha-olefin sulphonates and methyl ester sulphonates were not mineralized in lab anaerobic digesters despite the fact that the last one showed a certain degree of primary degradation. Nevertheless, these surfactants did not significantly inhibit methanogenic activity at concentrations up to 15 g surfactant/kg dry sludge, a concentration that is much higher than the expected concentrations of these surfactants in real anaerobic digesters. [redacted]

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1. Introduction

Sulphonates are one of the most widely used anionic surfactant groups in the household and personal care sectors. Apart from linear alkylbenzene sulphonates (LAS), the most important are alkane sulphonates in terms of volume. Moreover, alpha-olefin sulphonates, sulphosuccinates and alpha-sulpho fatty acid esters should also be taken into account (Porter, 1994; Hibbs, 2006). Secondary alkane sulphonates (SAS) consumption was estimated at about 72 kton in Western Europe in 2000, whereas the usage figures of the sulphosuccinates and alpha-olefin sulphonates (AOS), were 9 and 6 kton, respectively (Fraunhofer report, 2003). The consumption of methyl ester sulphonates (MES) is relatively low compared with the petrochemical-based surfactants LAS and SAS. However, given the sharp rise in oil prices, an increased interest in MES is expected.

SAS are water-soluble products that are fully resistant to hydrolysis even under extreme pH conditions (Steber and Berger, 1995). These surfactants are mainly used in light-duty liquid dishwashing detergents. AOS are in fact a mixture of alkene sulphonates (ca. 70%) and hydroxyalkane sulphonates (ca 30%). The properties of these products depend on the

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carbon chain length and on the ratio of the two classes of sulphonates present. The most important fields of application for AOS are laundry powders, light-duty dishwashing detergents and shampoos. Sulphosuccinic alkyl esters (mono or diesters) can be based on linear or branched alcohols and are sensitive to hydrolysis at acid and basic pH (Domingo, 1995). Although monoesters and diesters are excellent solubilising agents, diesters have an exceptional capacity to form microemulsions (Porter, 1994). Sulphosuccinates are used in special detergent formulations and personal care products. MES are chemicals of interest as detergent-range surfactants given that they are made from renewable natural raw materials, exhibit good washing properties and are stable to hydrolysis and are largely unaffected by water hardness (Domingo, 1995).

In terms of volume the most prominent field of application for these surfactants is their use in consumer products. After use, they are discharged into the environment through the sewage treatment infrastructure. Therefore, an understanding of their biodegradability and ecotoxicity is crucial for assessing the risk to the environment.

Available data on the ultimate aerobic biodegradation of SAS and AOS suggest that they are readily biodegradable (Swisher, 1987; Schöberl, 1988). In the Closed Bottle test 76% BOD/COD was found for MES (Gode et al., 1987) classifying this surfactant as readily biodegradable according to the OECD criteria (OECD, 1992). However, the data obtained for MES in the Sturm test (42–57% CO_2 evolution) by Schöberl et al. (1988) are below the limit of 60% mineralization in 28 days when methods based on respirometry are used. Aerobic biodegradation of sulphosuccinic alkyl esters is strongly influenced by the structural properties of the alkyl groups since branching of the alkyl moiety results in a fall in the primary biodegradation rate (Steber and Berger, 1995). Notwithstanding, data on the ultimate biodegradability of sulphosuccinates are scarce. Cordon et al. (1970) found an 83% DOC removal for di-octyl sulphosuccinate in a 3-week screening test. However, this surfactant was degraded only to a degree of 50% BOD/COD in the Closed Bottle test (Schöberl, 1988) with the result that it does not seem to be readily biodegradable according to the OECD criteria (OECD, 1992). Furthermore, little work has been done to elucidate the biodegradation routes of all these sulphonate-based anionic surfactants to date (Swisher, 1987; Steber and Wierich, 1989; Hales, 1993).

As for anaerobic biodegradability, no information exists in the literature about sulphosuccinic alkyl esters and very few data are available for SAS, AOS and MES, suggesting a poor biotransformation of these surfactants under anaerobic conditions (Steber and Wierich, 1989; Steber and Berger, 1995; Berna et al., 2007).

As regards ecotoxicity, SAS and AOS were found to be increasingly toxic to Daphnia magna as the alkyl chain length increased (Gerike, 1987; Schöberl, 1988) whereas no data are published on toxicity to aquatic organisms for MES and sulphosuccinates.

The purpose of this work is to assess for different sulphonate-based surfactants the effect of their structure on ecological properties such as the biodegradability under aerobic and anaerobic conditions and the toxicity to D. magna and Photobacterium phosphoreum.

2. Experimental

2.1. Surfactants

Five commercial sulphonate anionic surfactants were tested: an alkane sulphonate (sodium C_{14-17} sec-alkyl sulphonate, Hostapur SAS 30, 31% active matter, supplied by Clariant Ibérica S.A.), an alpha-olefin sulphonate (sodium alpha-olefin C_{14-16} sulphonate: a mixture of sodium alkene sulphonate (ca. 65%) and sodium hydroxyl alkane sulphonate (ca. 35%), Alfanox 46, 38% active matter, supplied by Kao Corporation S.A.), a methyl ester sulphonate (sodium methyl-2-sulpholaurate with <10% of disodium 2-sulpholaurate, Alpha-step MC-48, 38% active matter, supplied by Stepan S.A.), and two sulphosuccinates: a dialkyl sulphosuccinate (sodium bis(2-ethylhexyl)sulphosuccinate, Rewopol SBDO-70, 65% active matter) and a monoalkyl sulphosuccinate (disodium salt of sulphosuccinate monoester of dodecanol 3-mol ethoxylate, Rewopol SBFA-30, 39% active matter both supplied by Goldschmidt España S.A.). The surfactant structures and abbreviations used are given in Table 1.

2.2. Aerobic biodegradation test

The CO_2 headspace test (ISO 14593, 1999; OECD, 2006) was used to assess the aerobic biodegradability of the sulphonates. This method evaluates the ultimate biodegradation under aerobic conditions (mineralization to carbon dioxide) of an organic compound in an aqueous medium by measuring the increase in total inorganic carbon over time with respect to a blank without the addition of the test substance. The surfactants were tested at a concentration of 20 mg C/l. Samples were inoculated with activated sludge (10 mg dry solids/l) collected from a municipal wastewater treatment plant (Manresa, Barcelona) and then incubated in the dark at 22 ± 1 °C in 250 mL sealed vessels (air headspace/liquid volume ratio, 1:2). Sodium n-dodecyl sulphate was used as the positive control. Three replicates of the surfactants, blank and reference substance were performed for each sampling day. The tests ran for 28 days. On each sampling day, after injecting a sodium hydroxide solution to the vessels, shaking for 1 h and allowing to settle, appropriate volumes were withdrawn by syringe from the liquid phase of each vessel and kept in small beakers carefully filled to the brim and covered with a cap to prevent CO_2 exchange with the air. The concentration of inorganic carbon was determined in a carbon analyzer (Shimadzu TOC-5050). The biodegradation level was expressed as a percentage of the theoretical amount of inorganic carbon based on the initial amount of the test compound.

2.3. Anaerobic biodegradation test

A batch test system based on the method proposed by Birch et al. (1989) was employed. This method evaluates the ultimate anaerobic biodegradation of a chemical based on the production of biogas (methane and carbon dioxide) with respect to a blank without the addition of the test substance. Sludge samples from the anaerobic digester of a municipal wastewater treatment plant (Manresa, Barcelona) were used as inoculum.

Table 1 – Chemical structures and abbreviations of the surfactants tested.

Surfactant	Structure	Abbreviations
Secondary alkane sulphonates sodium C_{14-17} sec-alkyl sulphonate	$CH_3-(CH_2)_m-CH(SO_3Na)-(CH_2)_n-CH_3$ $n+m=11-14$	SAS
Alpha-olefin sulphonates sodium alpha-olefin C_{14-16} sulphonate (a mixture of sodium alkene and sodium hydroxyalkane sulphonates)	$CH_3-(CH_2)_m-CH=CH-(CH_2)_n-SO_3Na$ $+CH_3-(CH_2)_m-CH(OH)-CH_2-(CH_2)_n-SO_3Na$ (m + n = 11–13)	AOS
Methyl ester sulphonates sodium methyl 2-sulpholaurate (disodium 2-sulpholaurate < 10%)	$R-CH(SO_3Na)-C(=O)-OCH_3$ and $R-CH(SO_3Na)-C(=O)-ONa$ $R=C_{10-16}$	MES
Dialkyl sulphosuccinates sodium bis (2-ethylhexyl) sulphosuccinate	$NaSO_3CH(COOC_8H_{17})-CH_2COOC_8H_{17}$	di-C_8-SS
Monoalkyl ethoxy sulphosuccinates disodium salt of sulphosuccinate monoester of dodecanol 3-mole ethoxylate	$NaSO_3CH(COONa)-CH_2COO(CH_2CH_2O)_3C_{12}H_{25}$	$C_{12}(EO)_3$-SS

Total and volatile solids of the anaerobic sludge samples were determined according to Standard Methods (APHA, 1998) and the values obtained ranged from 30 to 50 g/l and from 45 to 60%, respectively. After collection, sludge was washed with a mineral salt solution, as described in the ECETOC (1998) test, to reduce the amount of inorganic carbon to a value < 10 mg/l. A final re-suspension step enabled adjustment of the dried solids concentration to 3 g/l. Four surfactant concentrations were tested for each surfactant (15, 35, 70 and 140 mg/g dry sludge for SAS, AOS, MES and di-C_8-SS and 15, 40, 85 and 170 mg/g dry sludge for $C_{12}(EO)_3$-SS). Each surfactant concentration was tested in triplicate. Glucose (100 mg C/L) was used as reference substance to check the procedure. Five replicates with anaerobic sludge but without any added surfactant were performed to determine the endogenous biogas production (control digesters). All samples were incubated in 250 mL pressure-resistant glass bottles at 36 °C ± 1 and the gas/liquid volume ratio was 3:7. The bottles were fitted with gas tight septa and aluminium crimp seals. After sealing the vessels and incubating them for about 1 h, excess gas was released to the atmosphere. Incubation proceeded in the dark. The resulting pressure was measured with a digital manometer connected to a syringe needle, and the increase in headspace pressure in the closed bottles was used to monitor the mineralization process. The incubation time was about 70 days. At the end of the test, after allowing the sludge to settle, appropriate volumes were withdrawn by syringe from the clear supernatant of each vessel and placed in small beakers carefully filled to the brim and covered with a cap to prevent CO_2 exchange with the air. The dissolved amount of the evolved carbon dioxide was determined as the concentration of inorganic carbon in the clear supernatant using a carbon analyzer (Shimadzu TOC-5050).

2.4. Surfactant analysis

Anionic surfactant analysis was carried out in the supernatant liquor and in the settled sludge of anaerobic digesters to determine the level of primary biodegradation. The surfactant extraction procedure was based on the method described by Matthijs and de Henau (1987). At the end of the biodegradation assays, aqueous and solid phases were separated by centrifugation at 4000 rpm for 15 min. Liquid samples: dissolved surfactant was concentrated by solid phase extraction using octadecyl (C_{18}) reversed phase silica columns (500 mg, J.T. Baker Inc., New Jersey). The anionic surfactant was eluted with methanol. The eluted solutions were then analysed to determine the anionic surfactant content. Solid samples: sludge samples from anaerobic digesters were dried at 105 °C and Soxhlet extracted with methanol for 8 h. These extracts were passed through a strong anion exchange column (Quart. Amine 500 mg, J.T. Baker Inc., New Jersey), eluted with methanol/HCl solution, neutralized and then passed over a C_{18} reversed phase silica column (500 mg, J.T. Baker Inc., New Jersey). The eluted (methanol) solutions were then analysed to determine the anionic surfactant content. The anionic surfactant content was determined by applying the Methylene Blue Active Substance (MBAS) spectrophotometric method (APHA, 1998). Surfactant quantification was conducted on the basis of specific calibration curves for each surfactant.

2.5. D. magna immobilization test

D. magna, laboratory bred, not more than 24 h old were used in this test (OECD, 2004), where the swimming incapability is the end point. The pH of the medium was 8.0 and the total hardness was 250 mg/l (as $CaCO_3$), with a Ca/Mg ratio of 4/1. Tests were performed in the dark at 20 °C. Twenty Daphnia, divided into four groups of five animals each, were used for each test concentration. For each surfactant, 10 concentrations in a geometric series were tested in the concentration range first established in a preliminary test. The percentage immobility at 48 h was plotted against concentration on logarithmic-probability paper and a linear relationship was obtained. The Probit Method was employed as the statistical procedure to determine the IC_{50} (the estimated concentration to immobilise 50% of the Daphnia after 48 h exposure) and the corresponding 95% confidence interval (CI). Statistical tests were performed in SPSS 15.0 for windows (SPSS, Chicago, IL, USA).

2.6. P. phosphoreum luminescence reduction test (Microtox test)

P. phosphoreum or Vibrio fischeri is a marine luminescent bacterium that liberates energy in the form of visible light (maximum intensity at 490 nm) as a consequence of a series of metabolic reactions. On exposure to toxic substances, the light output is reduced and this reduction is proportional to the toxicity of the sample. In the Microtox bioassay (DIN, 1997) the concentration of a chemical that causes a 50% reduction of the light emitted by the bacteria (EC_{50}) is estimated from a concentration–response curve by regression analysis. Toxicity data were based on a 30 min exposure of bacteria to the surfactant solution at 15 °C.

3. Results and discussion

3.1. Aerobic biodegradability

As stated above, the aerobic biodegradability of the sulphonate-based surfactants was assessed by performing the CO_2 headspace test (ISO 14593, 1999; OECD, 2006). This method is included in the European Regulation (EC) No 648/2004 on biodegradability of detergent surfactants and is the reference method for laboratory testing of ultimate aerobic biodegradability. A compound is considered to be readily biodegradable if the biodegradation level exceeds 60% within 28 days. It is assumed that such a chemical will be rapidly and completely biodegraded in aquatic environments under aerobic conditions.

The biodegradation curves obtained for the anionic surfactants tested are shown in Fig. 1. At the end of the test the degree of biodegradation of the sulphonates studied, calculated from the CO_2 production, exceeded 60% with the result that these surfactants can be regarded as readily biodegradable in the context of European Detergent Regulation (EC) 648/2004. Nevertheless, the level of mineralization was only 61% for MES, whereas it was about 80% for AOS, SAS and di-C_8-SS and more than 90% for $C_{12}(EO)_3$-SS. Although SAS and AOS achieved the same level of biodegradation, the

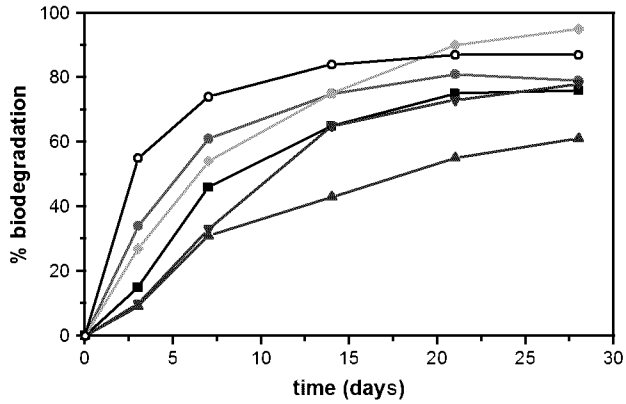

Fig. 1 – Aerobic biodegradation curves at a concentration of 20 mg C/l: (●) SAS, (-) AOS, (▲) MES, (▼) di-C_8-SS, (◆) $C_{12}(EO)_3$-SS, (B) SDS (positive control) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

biodegradation rate was higher for SAS than for AOS since 60% of the alkane sulphonate was already mineralized in the first week of the test whereas only 45% of the alpha-olefin sulphonate was biotransformed in the same period.

On the other hand, the results showed significant differences in the biodegradability of the tested sulphosuccinates as a function of the alkyl groups. Despite the fact that both compounds can be regarded as readily biodegradable, the biodegradation level at the end of the test was significantly higher for $C_{12}(EO)_3$-SS (>90%) than for di-C_8-SS (w80%). Biodegradation data suggest that the biodegradation of sulphosuccinates, initiated by the hydrolytic cleavage of the ester bonds (Hales, 1993), is followed by b-oxidation of the carboxylates formed from the alcohol residues. The structure of the released fatty acids would affect the biodegradation rate of the sulphosuccinate with linear alkyl residues ($C_{12}(EO)_3$-SS) exhibiting higher final degradation level than branched alkyl groups (di-C_8-SS). Therefore, it can be stated that branching of the alkyl moiety reduces the ultimate biodegradability of sulphosuccinates under aerobic conditions. Significant differences in ultimate biodegradation under aerobic conditions between branched and linear alkyl chains have been widely reported for alkylbenzene sulphonates (Swisher, 1987; Schöberl, 1988).

3.2. Aquatic toxicity assessment

The results of D. magna test and P. phosphoreum test for the surfactants tested are given in Table 2. The estimated concentration required to immobilise 50% of the freshwater crustacea population after 48 h of exposure (EC_{50}) ranged from 6 to 43 mg/l whereas the estimated concentration to reduce 50% of the light produced by the bacteria after 30 min of exposure (EC_{50}) ranged from 4 to 23 mg/l. These screening level toxicity data showed that the surfactants tested display a toxicity to D. magna similar to or lower than LAS (HERA-LAS, 2007), and in most cases there is no significant difference in the sensitivity of the two aquatic organisms to the toxic effects of

Table 2 – Acute toxicity of sulphonate-based surfactants to Daphnia magna and Photobacterium phosphoreum.

Surfactant	D. magna EC_{50}, 95% CI (mg/l)	P. phosphoreum EC_{50}, 95% CI (mg/l)
SAS	15 (14–16)	20 (11–34)
AOS	8.7 (7.7–9.7)	23 (17–32)
MES	6.6 (5.6–8.1)	4.8 (2.5–8.5)
di-C_8-SS	43 (34–55)	15 (6–35)
$C_{12}(EO)_3$-SS	9.7 (8.4–11)	12 (11–13)

these anionic surfactants. Given that the methyl ester sulphonate was the most toxic and the dialkyl sulphosuccinate was the least toxic to the aquatic organisms tested, no effect due to the presence of an ester bond in the molecule on the toxicity to freshwater crustacean and luminescent bacteria was found. Both sulphosuccinates exhibited a similar toxicity to P. phosphoreum whereas against D. magna the monoalkyl sulphosuccinate was less toxic. However, it cannot be concluded that the lower toxicity to freshwater crustacean of di-C_8-SS is due to branching of the alkyl moiety because this surfactant has two alkyl chains and these are shorter than the alkyl chain of $C_{12}(EO)_3$-SS. An increase in toxicity to D. magna with the alkyl chain of the surfactant is a usual finding that has been widely reported for LAS homologues (HERA-LAS, 2007) and already mentioned in Section 1 for SAS and AOS.

3.3. Anaerobic biodegradability and toxicity

The biodegradability of sulphonate-based surfactants and their effects on the anaerobic digestion process of sludge were investigated by performing batch degradation tests at surfactant concentrations ranging from 20 to 200 mg C/l that correspond approximately to 15–150 g surfactant/kg dry sludge. The surfactant concentrations higher than 20–50 mg C/l, which are the values recommended in the biodegradation test, were tested to assess the potential toxicity of these compounds to anaerobic microorganisms.

3.3.1. Primary biodegradation

Primary biodegradation of the sulphonate-based anionic surfactants in the anaerobic tests was calculated from the overall mass balance of anionic surfactant in the digesters. To this end, the anionic surfactant content was determined by MBAS analysis in liquid and solid phases at the beginning and end of the degradation tests in control digesters and the digesters spiked with different surfactant concentrations. The percentages of surfactant removal are given in Table 3.

Table 3 – Primary biodegradation of the sulphonate-based anionic surfactants in the anaerobic tests.

Surfactant	Primary biodegradation (%) Mean ± SD
SAS	12 ± 2
AOS	10 ± 4
MES	44 ± 6
di-C_8-SS	73 ± 7
$C_{12}(EO)_3$-SS	76 ± 7

For SAS and AOS, the percentages of removal ranged from 10 to 12%, which is consistent with the data reported for LAS mass balance over full scale anaerobic digesters (0–35%) in monitoring studies (Berna et al., 1989), and in laboratory batch digesters (0–12%) (Garcia et al., 2006a). The low degree of surfactant removal obtained for alkane and alpha-olefin sulphonates shows that the microbial transformation of these compounds under the conditions of the anaerobic screening tests is not significant as reported in an earlier work for LAS, the most common sulphonate-based surfactant (Garcia et al., 2006b). The persistence of SAS and AOS under anaerobic conditions would agree with a mechanism of hydrophobic oxidation of the molecule as the main degradative pathway for these surfactants. The slight surfactant depletion observed could be attributed to some oxygen diffusion in the handling of sludge samples in the initial steps of the experiments, resulting in a small degree of surfactant biodegradation initiated by the u-oxidation mechanism.

For the two sulphosuccinates high percentages of surfactant removal (| 70%) were found in the anaerobic digesters whereas the primary degradation of MES was only about 40%.

Differences between SAS, AOS, MES and sulphosuccinates can be attributed to their molecular structure. The ester bonds in the sulphosuccinates are easily hydrolysable either chemically or enzymatically. This enables cleavage into non-surface active fragments and is consistent with the high primary biodegradation found in the anaerobic digesters. For MES, the stabilization of the ester bond by the adjacent sulphonate group leads to a lower degree of primary degradation of the surfactant (40%) in comparison with sulphosuccinates (| 70%). Finally, the requirement of molecular oxygen for the u-oxidation, which seems to be the main degradative pathway for SAS and AOS biological degradation, would account for their negligible removal in anaerobic environments.

3.3.2. Ultimate biodegradation and toxicity

The evolution of biogas production in the digesters spiked with different surfactant concentrations for the anionic surfactants studied is plotted in Fig. 2.

For SAS, AOS and MES (Fig. 2), the biogas production was lower than the production of biogas in the control digesters (endogenous biogas production). Therefore, these surfactants were not mineralized in anaerobic digesters. The inhibition of biogas production caused by these compounds, as a measure of their toxicity to the anaerobic microorganisms, was calculated by comparing the biogas production in the anaerobic digesters spiked with different surfactant amounts and the endogenous biogas production at the end of the test period. Results are plotted in Fig. 3.

For SAS, AOS and MES, the inhibition of the anaerobic activity increased with the surfactant concentration. At the lowest concentration tested (15 g/kg dry sludge), the inhibition of biogas produced by SAS and AOS was lower than 10% whereas MES showed a biogas production inhibition >20% (Fig. 3). Nevertheless, it is worth to remark than even LAS, which is used at much higher tonnages, is not commonly found at such high concentrations as 15 g/kg dry sludge. At higher surfactant concentrations, the inhibition of anaerobic activity increased more dramatically for SAS and AOS than for MES. Thus, at surfactant concentrations | 35 g/kg dry

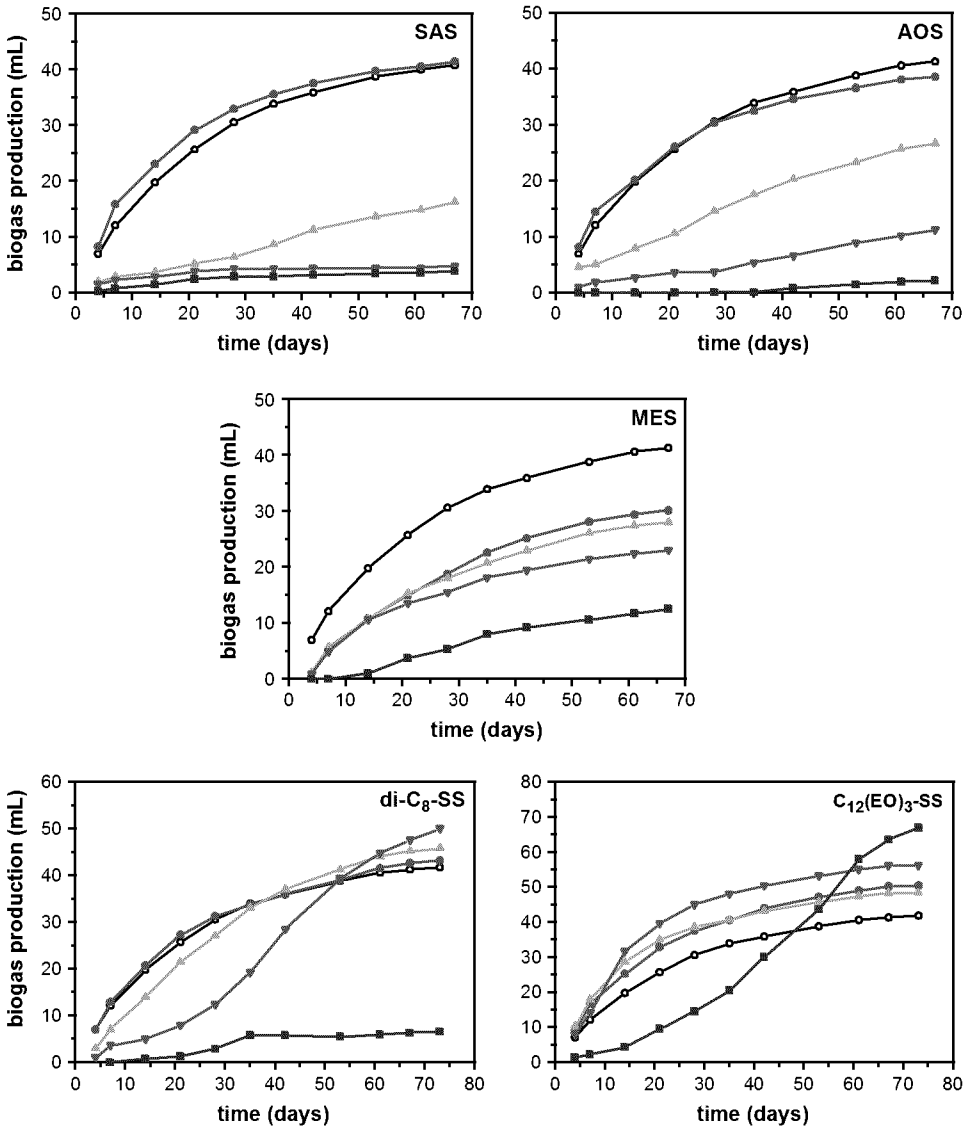

Fig. 2 – Evolution of biogas production in the anaerobic digesters spiked with SAS, AOS, MES and di-C_8-SS at (●) 15 mg surfactant/g dry sludge, (▲) 35 mg surfactant/g dry sludge, (▼) 70 mg surfactant/g dry sludge, (■) 140 mg surfactant/g dry sludge, with $C_{12}(EO)_3$-SS at (●) 15 mg surfactant/g dry sludge, (▲) 40 mg surfactant/g dry sludge, (▼) 85 mg surfactant/g dry sludge, (■) 170 mg surfactant/g dry sludge and (B) in control digesters. Biogas production was calculated at standard temperature and pressure. The standard deviation of experimental data ranged from 2 to 14% (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

sludge, the most severe effects on biogas production were observed for SAS and AOS (Fig. 3). Both surfactant produced a practically complete inhibition of biogas production at concentrations ¦ 70 g/kg dry sludge whereas the inhibition caused by MES did not exceed 65% even at the highest concentration tested, 140 g/kg dry sludge. The toxicity of these surfactants to the anaerobic microorganisms, calculated from the reduction of the maximum biogas production at each surfactant concentration, was expressed as the estimated surfactant concentration to reduce the biogas production by 50% (EC_{50}). The EC_{50} values were 35, 40 and 70 g surfactant/kg dry sludge for SAS, AOS and MES, respectively.

Given that the expected concentrations of SAS, AOS and MES in anaerobic sludge of WWTPs are much lower than the average background concentration reported for LAS (w4 g/kg dry sludge) (Garcia et al., 2006b), no toxic effects are expected in real anaerobic digesters attributable to the presence of these compounds.

As for the sulphosuccinates tested, the biogas production in digesters spiked with di-C_8-SS (Fig. 2) was higher than the endogenous biogas production at the end of the test period, and increased with the surfactant concentration up to 70 g/kg dry sludge. The percentage of mineralization obtained for di-C_8-SS at 15, 35 and 70 g/kg dry sludge ranged from 35 to 50%. The inhibition and recovery of the biogas production at

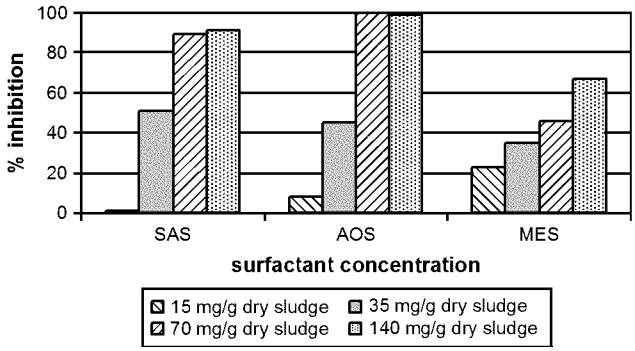

Fig. 3 – Inhibition of anaerobic activity in the digesters spiked with SAS, AOS and MES.

the latter surfactant concentration could be attributed to adaptation of anaerobic microorganisms after a period of 50 days. At a concentration of 140 g/kg dry sludge, however, no recovery of the anaerobic activity was observed. In digesters spiked with $C_{12}(EO)_3$-SS (Fig. 2) the biogas production at the end of the test period was significantly higher than in control digesters even at highest surfactant concentration tested, 170 g/kg dry sludge. The percentages of ultimate biodegradation of $C_{12}(EO)_3$-SS were ¦80% for surfactant concentrations up to 85 g/kg dry sludge and 23% at 170 g surfactant/kg dry sludge. Despite extensive anaerobic biodegradation occurred for $C_{12}(EO)_3$-SS (¦80% of the theoretical biogas production was achieved when tested at the recommended concentrations in this test) it cannot be concluded that mineralization of the surfactant is complete without further investigation on the fate of the sulphonate moiety.

Likewise, $C_{12}(EO)_3$-SS exhibited a very low toxicity to the methanogenic microorganisms given the increase in biogas production at a surfactant/biomass ratio as high as 170 g/kg dry sludge after an adaptation period. It is worth to remark that despite the surfactant concentration was two times higher, the adoption period of anaerobic microorganisms to the monoalkyl sulphosuccinate was the same than for the dialkyl sulphosuccinate (50 days).

The anaerobic ultimate biodegradation of sulphosuccinates can be attributed to the molecular structure of these surfactants. Cleavage of ester bonds takes place via either chemical or microbial processes to yield fatty acids and sulphosuccinic acid. This initial step does not require molecular oxygen and could therefore take place under anaerobic conditions as suggested by the high level of primary degradation obtained (>70%). Released fatty acid molecules can undergo biodegradation via b-oxidation. However, the presence of branched alkyl chains could hinder this mechanism. The experimental results lend support to this assumption since ultimate biodegradation percentages ¦80% were found for the linear alkyl sulphosuccinate ($C_{12}(EO)_3$-SS) whereas the mineralization degree was ¬50% for the branched alkyl sulphosuccinate (di-C_8-SS). Therefore, under anaerobic conditions – as was also stated for aerobic conditions – branching of the alkyl moiety results in a reduction in the ultimate biodegradability of sulphosuccinates.

4. Conclusions

Alkane sulphonates, alpha-olefin sulphonates, methyl ester sulphonates and sulphosuccinates (mono and dialkyl) are biodegraded under aerobic conditions. However, only sulphosuccinates will be partially (branched alkyl sulphosuccinates) or extensively (linear alkyl sulphosuccinates) mineralized in anaerobic digesters given that the ester linkage and its position with respect to the sulphonate group are essential for the degradation of the surfactant molecule under anaerobic conditions. On the other hand, no clear effect of the structural properties of the sulphonate-based surfactants on their toxicity to the aquatic organisms tested (D. magna and P. phosphoreum) is observed.

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Degradation of Dispersants and Dispersed Oil

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Introduction

Chemical oil dispersants are proprietary mixtures of surfactants and solvents which are directly applied to a spill in order to reduce the natural attractive forces of the oil. When oil treated with dispersants is exposed to mixing energy, typically from wind and wave action, it is broken up in to small droplets which may then become entrained in the water column (Li et al., 2009a; Li et al., 2009b ; Li, 2008; Lunel, 1995). Many of these droplets are small enough to be neutrally buoyant, and therefore, advection and diffusion forces dilute the plume and transport the droplets far from the site of the original spill. As compared to a surface oil slick or larger and more buoyant physically dispersed oil droplets, these chemically dispersed droplets are much easier for oil-degrading bacteria to colonize and break down (Venosa and Holder, 2007; Venosa and Zhu, 2003). In addition, small droplets enhance dissolution of soluble and semi-volatile compounds into surrounding waters, wherein biodegradation is carried out by aqueous phase microbes. Under these conditions, oil concentration are effectively reduced below toxicity threshold limits, and biodegradation becomes the most important process in reducing the total mass of petroleum hydrocarbons in the environment. By enabling rapid dispersion and biodegradation of surface oil slicks at sea, the use of chemical oil dispersants can be effective in preventing heavy oiling of sensitive coastal environments such as beaches and wetlands, and consequently mitigates risk associated with marine and terrestrial wildlife coming into direct contact with a slick.

Biodegradation of Oil

Any discussion on the biodegradation of chemically-dispersed oil must consider the degradation of the oil itself. A variety of microorganisms in both terrestrial and marine environments have the capacity to utilize petroleum hydrocarbons as the sole source of carbon and energy (Head et al., 2006 ; Leahy and Colwell, 1990; Atlas, 1981 , 1984 ; ZoBell, 1973). Recently a 181 genera of bacteria, 163 genera of filamentous fungi and yeast, and 22 genera of algae have been identified to have the ability to degrade hydrocarbons by metabolizing them in order to grow (Prince, 2010 a,b). These findings are not surprising considering the fact that marine microorganisms have long been exposed to significant quantities of petroleum hydrocarbons from natural seepages.

From 1990 to 1999, approximately 600,000 tons of petroleum were released into the world's oceans per year from natural seepages (NRC, 2003; Stout and Wang, 2008) . Biodegradation by indigenous microbial communities is the major process responsible for the weathering and eventual removal of oil from natural seeps that enters the marine

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environment (Atlas, 1995; Atlas and Bartha, 1992; Leahy and Colwell, 1990). Within the marine environment, bacteria are the predominant hydrocarbon degraders (Head et al., 2006; Venosa and Zhu, 2003). Studies from tropical to cold Antarctic and Arctic environments have verified their ubiquitous distribution and their ability to multiply rapidly upon the introduction of oil (Atlas, 1995).

Biodegradation rates have been shown to be the highest for saturates, followed by light aromatics, with high-molecular-weight aromatics and polar compounds exhibiting extremely low biodegradation rates (Prince, 2010c). Co-metabolism plays an important role in oil biodegradation and may require microbial consortia or syntrophic interspecies cooperation (McInerney et al., 2008). Many complex branched, cyclic, and aromatic hydrocarbons, which otherwise would not be biodegraded individually, can be oxidized through co-metabolism in an oil mixture due to the abundance of other substrates that can be metabolized easily within the oil (Atlas, 1981).

It is important to note that microorganisms produce extracellular biosurfactants to promote the formation of oil-in-water emulsions that aid in the uptake and subsequent degradation of hydrocarbons (Desai and Banat, 1997). The hydrophilic and hydrophobic components within the biosurfactants emulsify hydrophobic hydrocarbons, and allow for transport into the hydrophilic intracellular space for biodegradation (Southam et al., 2001). In addition, the fatty acid moieties of biosurfactants promote the growth of microorganisms on the surface of oil droplets (Rosenberg et al., 1979). Nikolopoulou and Kalogerakis (2008) reported that the use of rhamnolipid biosurfactants increased removal of weathered petroleum hydrocarbons (96% removal of C19–C34 n-alkanes within a period of 18 days) and reduced the lag phase prior to the onset of biodegradation. Saeki et al. (2009) showed that addition of biosurfactant JE1058BS to seawater stimulated the degradation of weathered Alaska North Slope 521 crude oil by stimulating the activity of the indigenous marine bacteria and facilitating the removal of oil from the surface of contaminated marine sediments.

In terms of the influence of environmental factors controlling natural oil biodegradation rates, field studies have shown that active microorganisms living in low-temperature environments are dominated by two groups: psychrophilic and psychrotolerant, which are sometimes called psychrotrophic (Atlas, 1984). As defined by Morita (1975), psychrophiles experience optimum growth at less than 15°C, with a maximum growth temperature below 20°C and a minimum growth temperature at or below 0°C. Despite living at these low temperatures, psychrophiles often have metabolic rates comparable to those displayed by the mesophiles adapted to more moderate temperatures. For example, Delille et al. (2009) reported that a temperature of 4°C in the Antarctic had little effect on biodegradation efficiency and that the nutrients, nitrogen and phosphorus, were the limiting factors. Results obtained by Siron et al. (1995) indicated that the temperature threshold for observing significant oil biodegradation was around 0°C. Decreases in solubility associated with low temperatures were considered to be a causal factor for the cases of observed recalcitrance of hydrophobic compounds in cold-water. However, recent reports have indicated that some bacteria may have adapted to the low solubility of hydrophobic environmental chemicals (Deppe et al., 2005; Wick et al., 2002). Indeed there is now evidence that hydrocarbon-degrading microbes may have novel uptake

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mechanisms that enable them to degrade hydrocarbons at rates that exceed their r ates of dissolution in the aqueous phase (Leahy and Colwell, 1990; Thomas et al., 1986).

Throughout the world, the salinity of seawater averages about 35 ‰ (parts per thousand). Salinity variations, albeit small, are mainly caused by such factors as melting of ice, inflow of river water, evap oration, rain, snowfall, wind, wave action, and ocean currents that cause horizontal and vertical mixing of the saltwater (Lagerloef et al., 1995) . Most marine species have an optimum salinity range of 25 –35‰ (ZoBell, 1973) and speci es living in the transition environments are well adapted to fluctuations in salinity. Microorganisms requiring salt for growth are referred to as halophiles. Whereas halophilic hydrocarbon -metabolizing bacteria perform well in this salinity range, there have been reports of the isolation of bacteria capable of degrading hydrocarbons above a salinity of 35 ‰. Bertrand et al. (1990) reported the isolation from a sal t marsh of an extremely halophilic archaea bacterium capable of degrading hydrocarbons in 204 ‰ NaCl, but not below 105 ‰. Diaz (2008) reported the isolation of a bacterial consortium, which mainly included members of the genera *Marinobacter*, *Erwinia* and *Bacillus*, from a crude oil sample from the Cormorant field in the North Sea. This consortium was able to metabolize petroleum hydrocarbons in a salinity range from 0 to 220 ‰ NaCl. Total oil degradation ranged from 48% to 75%, with the greater degradation occurring at the lower salinities.

At the sea surface, wind and wave action maintain a constant supply of o xygen, thus aerobic catabolism of hydrocarbons is usually the preferred biochemical pathway (Leahy and Colwell, 1990) . Oxygen may become limiting in subsurface sediments and anoxic zones of the water column. Oxygen limitation is also a concern for most fi ne-grained marine shorelines, freshwater wetlands, mudflats and salt marshes (Venosa et al., 2002a; Venosa and Zhu, 2003). It is commonly believed that biodegradation rates under anaerobic conditions are almost negligible, while aerobic biodegradation of hydrocarbons occurs rapidly. However, the importance of anaerobic biodegradation should not be underestimated as it has been shown to be a major process under certain conditions. In anoxic marine sediments, reductions of sulphate, Mn(IV) and Fe(III) are the primary terminal electron-accepting processes (Canfield et al., 2005; Finke et al., 2007). Hydrocarbon degradation coupled with sulphate reduction prevails in marine anoxic sediments (Lovley et al., 1997).

With recent advances in analytical methods such as genomics, we are now able to determine the potential of whole microbial communities for oil biodegradation at low temperatures. New evidence as a result of advances in the field of environmental genomics suggests that crude oils are degraded by indigenous organisms in cold water environments at a higher rate than previously reported. This is not surprising since natural oil seeps occur in the world's o ceans at great depths and low temperatures – microbes have become well adapted to their surrounding environment. S tudies have conclusively shown that elevated concentrations of hydrocarbons in the environment increase the number of catabolic -gene copies a mong the microbial community (Heiss-Blanquet et al., 2005; Stapleton and Sayler, 2000; Whyte et al., 2002).

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Biodegradation of Chemically Dispersed Oil

The effect of chemical dispersion on the biodegradation rate of petroleum hydrocarbons has been studied for several decades, and it is generally agreed that chemically dispersed oil is biodegradable. However, the observed effects of chemical dispersants on the rate of oil biodegradation have varied significantly among studies (National Research Council, 2005). Whereas some studies observed stimulation of biodegradation rates by the use of chemical dispersants (Swannell and Daniel, 1999; Traxler and Bhattacharya, 1978), chemical dispersion inhibited the biodegradation rate or had no effect in other studies (Foght and Westlake, 1982; Lindstrom and Braddock, 2002). The effect of chemical dispersion on the rate of oil biodegradation has been further complicated by substrate-dispersant interactions associated with differences in the experimental test conditions, which caused the biodegradation of individual hydrocarbons to be stimulated by some dispersants and inhibited by others (Foght et al., 1987; Van Hamme and Ward, 1999). As a result, it is difficult to predict the effect of dispersants on the biodegradation of specific hydrocarbons based on chemical class (e.g., aliphatic vs. aromatic) (Foght et al., 1987; Lindstrom and Braddock, 2002). Similarly, the effects of specific dispersants on biodegradation cannot be predicted based on the chemical characteristics of the surfactants or the hydrophile-lipophile balance (HLB) of the mixture (Van Hamme and Ward, 1999; Varadaraj et al., 1995).

Attempts have been made to predict the rate of oil biodegradation in the environment based on the results of laboratory studies using scalable, quantitative biodegradation kinetics models that treat oil as droplets suspended in water rather than as homogenous solutions of hydrocarbons in water and consider the growth of the organisms responsible for the biodegradation of oil (National Research Council, 2005). To date only two studies have made an attempt to estimate biodegradation kinetic parameters (Venosa and Holder, 2007; Zahed et al., 2011), by measurement of first-order (in oil concentration or the concentrations of specific oil components) rate coefficients to enable comparison among treatments. However as only one independent rate coefficient was estimated for each treatment, treatment effects could not be rigorously evaluated.

Conducting representative biodegradation studies on dispersed oil in microcosm-scale test systems has at least two important challenges that researchers need to consider as they develop test protocols (Lee et al., 2011). One challenge is to conduct tests at the low dispersed oil concentrations representative of field conditions. Many previous biodegradation studies were conducted at unrealistically high concentrations of dispersed oil in closed microcosms. Prior research either failed to recognize the rapid dilution that occurs at sea or employed methods that were not sufficiently sensitive to study low concentrations. Studying dispersed oil biodegradation at concentrations several orders of magnitude above expected at-sea concentrations in closed systems could limit biodegradation rates and total degradation by exhausting the available nutrients. Some researchers attempted to address this by adding nutrients to the system, but this can lead to unrepresentative modification of the microbial community.

The second challenge with studying dispersed oil biodegradation in a closed system is the difficulty of maintaining a stable dispersion in the laboratory. Dispersed oil in the water

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column exists as small droplets that neither surface nor sink, and the droplets beco me so scattered that they cannot coalesce. It is challenging to maintain stable dispersions of oil in closed systems during the often multi-week test periods required to conduct biodegradation studies. To simulate the dispersion of oil at sea, biodegradati on studies require formation of a stable dispersion containing droplets no greater than 70 - 100 microns and enough mixing energy to keep droplets from resurfacing during an experiment.

A recent Joint Industry Program (McFarlin et al., 2011) on the biodegradation of oil under Arctic conditions has assessed biodegradation of chemically and physically dispersed Alaska North Slope oil as indicated by both primary degradation and hydrocarbon mineralization. The study was conducted under low ambient temperature conditions (-1oC – 2oC) and relatively low oil concentrations (10 -12 ppm crude oil in seawater) and under low level nutrients (0.5 – 1% of the OECD recommended volume of Bushnell Haas Broth). The results of the study demonstrated that the use of dispersant increased the primary biodegradation of fresh oil from 37% to 56% and the mineralization from 12% to 27%. Further increment w as due to the addition of nutrients by 10 % for both primary degradation and mineralization.

Biodegradation of Dispersants

Most studies on surfactant biodegradation focus on surfactants that are used in high - volume consumer products, such as laundry deterg ents (e.g., linear alkyl sulfonates), or other cleaning agents which have known environmental health and safety concerns (e.g., alkylphenol ethoxylates). In general, the results of these have shown that most surfactant formulations are fairly readily biode graded under aerobic (oxygen present) conditions by marine bacteria (Lee et al., 1985; Liu, 1983; Una and Garcia, 1983). The rate of biodegradation under anaerobic (absence of oxygen) conditions tends to be much lower (Berna et al., 2007; Ying, 2006). [redacted] Through the use of anaerobic digesters and analyses of bacterial biogas production, Garcia et al. (2009) conducted a series of batch degradation experiments which revealed that the anaerobic biodegradability of branched alkyl sulphosuccinates such as those used in Corexit were much lower (≤50% mineralization after 50 days) than that of lin ear alkyl sulphosuccinates (≥ 80% mineralization after 50 days). It is clear that different types of surfactants, and even individual surfactants of the same class, can biodegrade at very different rates depending on the structural complexity of chemical branching.

A report by the Fraunhofer Institute (2003) discusses in detail the anaerobic biodegradation of detergent surfactants such as those used in household cleaners. Unfortunately, little attention is paid to the surfactants commonly found in chemical oil dispersants. Generally speaking, the report states that non -ionic surfactants are readily biodegradable under both aerobic and anaerobic con ditions. [redacted]

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The biodegradation of surfactants used oil spill treatment agents h as been studied fo r years (Baumann et al., 1999; García et al., 2009; Lindstrom and Br addock, 2002; Liu, 1983; Odokuma and Okpokwasili, 1992; Una and Garcia, 1983). Surfactant biodegradation studies usually distinguish between primary biodegradation, which was calculated from the overall mass balance of surfactant in the reactors (García et al., 2009; Una and Garcia, 1983), and ultimate biodegradation, which also considers the removal of the intermediate products, usually based on oxygen consumption (Odokuma and Okpokwasili, 1992) or carbon dioxide production (García et al., 2009; Lindstrom and Braddock, 2002) relative to the amount expected based on the compound structure. [redacted] (Una and Garcia, 1983). Primary biodegradation of Span 80, the unethoxylated non-ionic surfactant used in both Corexit products, was less than 20% in the same study, but the authors suggested that the poor biodegradation may have been caused by subst rate inhibition due to the extremely [redacted] Ultimate biodegradation of Tween 80 was about 50% in another study (Baumann et al., 1999) , and [redacted] (García et al., 2009), but the observed oxygen consumption or carbon dioxide production were much lower than expected for Corexit 9527 (Odokuma and Okpokwasili, 1992) and Corexit 9500 (Foght et al., 1987), respectively, suggesting that biodegradation was incomplete within the testing period. Some studies have suggested that partial biodegradation of Tween 80 involves metabolism of the oleic acid portion of the molecule, leaving the polyethoxy groups untouched or only partially metabolized (Baumann et al., 1999; Kim and Weber Jr., 2003). Note, however, that enzymatic oxidation and subsequent metabolism of polyethoxylate groups has been described (Nguyen and Sigoillot, 1997; Owen et al., 1997).

[redacted] Unfortunately, until the recent Deepwater Horizon oil spill in the Gulf of Mexico, little information is available on the fate of surfactants in the presence of natural microbial seawater communities at concentrations expected during actual spill response operations. .

Toxicity and Bioaccumulation of Dispersant Surfactants

The toxicity of dispersants may influen ce trophic level dynamics including microbial processes responsible for oil degradation (Lee et al,, 1985). The premise of dispersant use is based on the reduction of oil to concentrations be low toxicity threshold limits. Based on the results of toxicity tests for EPA-approved dispersants such as Corexit 9527 and 9500 listed on the National Contingency Plan (NCP) Product Schedule and the

recommended dispersant-to-oil (DOR) application rates, major environment impacts were not expected at the concentrations to be encountered during their operational use for the treatment of oil spills. A report from the Centers for Disease Control and Prevention (2010) also concluded that "because of the strict guidelines that must be followed to utilize dispersants, it is unlikely that the general public will be exposed (directly) to (the) product." The report further states that "ingredients are not considered to cause chemical sensitization; the dispersants contain proven, biodegradable and low toxicity surfactants."

Despite the development of a regulatory approval mechanism for the support of their operational use, a considerable amount of ongoing research has been funded to evaluate the toxicity of chemical oil dispersants in the marine environment . Public concerns remain high in regards to this topic as the data collected to date has been highly variable due to factors such as differential sensitivity between species, the particular dispersant formulation used, and experimental conditions used (George-Ares and Clark, 2000; Lyons et al., 2011).

Ramachandran et al. (2004) reported that chemically-dispersing different crude oils increased the exposure of fish to the constituents of oil by 10 to 1000-fold in comparison to undispersed oil. The enhanced exposure was demonstrated by an increased activity of liver enzymes that oxygenate compounds accumulated from water containing chemically-dispersed oil droplets. The implication of this work is that the toxicity of oil to fish increased following chemical dispersion in proportion to the extent to which the oil was dispersed. It was noted that the amount of a solution of chemically-dispersed oil that caused toxicity was 100 times less than the amount of undispersed oil required to cause the same effect. However, the measured concentrations of hydrocarbons that were toxic was virtually the same between solutions of dispersed and undispersed oil. Thus, the effect of chemical dispersion was to transfer more compounds from oil to water, and not to make these compounds more toxic.

A study conducted by Fuller et al. (2004) using two fish species, *Cyprinodon variegatus* and *Menidia beryllina*, one shrimp species, *Americamysis bahia* (formerly *Mysidopsis bahia*), and the luminescent bacteria *Vibrio fisherithese* indicated that the toxicity of chemically dispersed oil preparations was equal or less toxic than that of the oil alone. A separate study by Hemmer et al. (2010) looking at toxicity of Louisiana Sweet Crude (LSC), chemical oil dispersants, and chemically dispersed LSC on *M. beryllina*, and *A. bahia* reported that the toxicity of the dispersant alone was lower than that of LSC or dispersed LSC which both showed moderate to high toxicity. Similarly, Milinkovitch et al. (2011) found that while containment and recovery of spilled oil is optimal, there is no significant difference between the toxicity of naturally and chemically dispersed oil when looking at a series of biomarker responses in the gills of golden grey mullet (*Liza aurata*). Further work by Judson et al. (2010) has investigated the potential for chemical oil dispersants to interfere with hormone and other bio-chemical processes in marine organisms. The results of this study concluded that while some dispersants did show low potential for endocrine disruption, most (including Corexit) did not show any significant effect.

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Brief pulses of chemically-dispersed oil can be just as toxic to fish embryos as prolonged exposures. McIntosh et al. (2010) recently reported that exposures to chemically-dispersed crude oil as brief as one hour prevented the fertilization of Atlantic herring embryos. Similarly, one -hour exposures immediately following egg fertilization were sufficient to cause deformities, interfere with development, and kill herri ng embryos at oil concentrations typical of those measured near actual marine oil spills. Thus, contrary to expectations, the primary concern about oil dispersion may not be the toxicity of chemical dispersants, nor the enhanced toxicity of oil. Rather, it is the greatly increased exposure of highly sensitive embryos to the toxic components of oil. As the result, there is the possibility that even brief exposures of fish embryos to dispersed oil can cause embryo toxicity at oil concentrations typical of actual spills. The results of these laboratory studies have highlighted the need for future research to determine effects under the environmental conditions encountered under operational response operations.

In light of the toxicity research study results obtained for chemical oil dispersants, it is suggested that factors such as toxicity of dispersed oil (rather than dispersant itself), dilution and degradation in the environment, species/resources requiring priority protection, potential adverse effects of all response options, and the potential for recovery of sensitive habitats and populations should weigh more heavily into the decision making process than dispersant toxicity alone George-Ares and Clark (2000). Supporting this view, a recent review of the use of chemical dispersants in Europe found that ongoing improvement in dispersant formulation has now reached a point where the toxicity of the dispersant itself is much less important than the toxicity of the oil it is dispersing (Chapman et al., 2007).

While the focus of studies on chemically dispersed o il has been on the induction of acute and/or chronic toxic effects for risk assessments associated with dispersant use, some consideration has also been given to the bioaccumulation of surfactants. In a study on the uptake of two linear alkylbenzene sulfo nates by a freshwater oligocheate (*Lumbriculus variegatus*) and a larval insect (*Chronomus riparius*) using radioactive tracers Mäenpää and Kukkonen (2006) reported that the surfactant residue in the body of the test organisms was more highly dependent on the organic content of the test sediment than on the initial exposure concentration . It was concluded that the high organic content of the test sediment reduced body residue concentrations due to the adsorption of the surfactant to the organic material cont ained in the sediment. This result is consistent with earlier research that concluded surfactants of all classes are readily taken up across the gills but that environmental variables could reduce the concentration of surfactants associated with the test species (EOSCA, 2000).

Following a comprehensive review on the bioaccumulation potential of surfactants , the European Oilfield Specialty Chemicals Association (EOSCA) concluded that although surfactants and their metabolites can be found in aquatic organisms following exposure, there is no evidence to support biomagnification of surfactants through the food chain (EOSCA, 2000). There is also evidence that non-ionic and anionic surfactants (such as those found in most oil dispersants) are biotransformed and eliminated via the gall bladder (Tolls et al., 1994) As a result of surfactant metabolism , Comber et al. (2003)

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suggested that linear alkylbenzene sulfo nates, alcohol ethoxylates, and other structurally similar surfactants are unlikely to bioaccumulate to any significant degree.

Dispersant Use During the DWH Spill Response

The decision by the EPA, NOAA and BP to use chemical dispersants at the Deepwater Horizon spill site did not come lightly. The United States Clean Water Act specifically addresses the use of dispersants in response to oil spills in Section 311(d)(2)(G) which requires that the federal National Contingency Plan for oil spill response contain a schedule identifying:

> (i) dispersants, other chemicals, and other spill mitigating devices and substances, if any, that may be used in carrying out the Plan,
>
> (ii) the waters in which such dispersants, other chemicals, and other spill mitigating devices and substances may be used, and
>
> (iii) the quantities of such dispersant, other chemicals, or other spill mitigating device or substance which can be used safely in such waters, which schedule shall provide in the case of any dispersant, chemical, spill mitigating device or substance, or waters not specifically identified in such schedule that the President, or his delegate, may, on a case -by-case basis, identify the dispersants, other chemicals, and other spill mitigating devices and substances which ma y be used, the waters in which they may be used, and the quantities which can be used safely in such waters.

Although Corexit 9527 and 9500 were both pre-approved by the EPA for use in the event of an oil spill, until the incident in the Gulf, little consideration was given to the suitability of these products for subsurface application. Subsurface injection of dispersant was considered as a means to reduce VOC levels and the volume of dispersant to be used (as application at the well head would improve con tact between dispersant and the oil). Thus, regulatory approval subsurface application was withheld until its efficacy and potential effect on the environment could be assessed (EPA Press Conference Call, 2010).

Following a Net Benefit Environmental Analysis (NEBA) process, a decision was made to apply dispersions an operational countermeasure during the Deepwater Horizon response operations. In Total, 43,884 barrels of Corexit brand chemical oil dispersant was applied (1); 25,505 barrels of Corexit 9527 and Corexit 9500A at the surface (by spraying from vessels at sea and aircraft) and 18,379 barrels of Corexit 9500 via subsurface injection (Federal Interagency Solutions Group, 2010).

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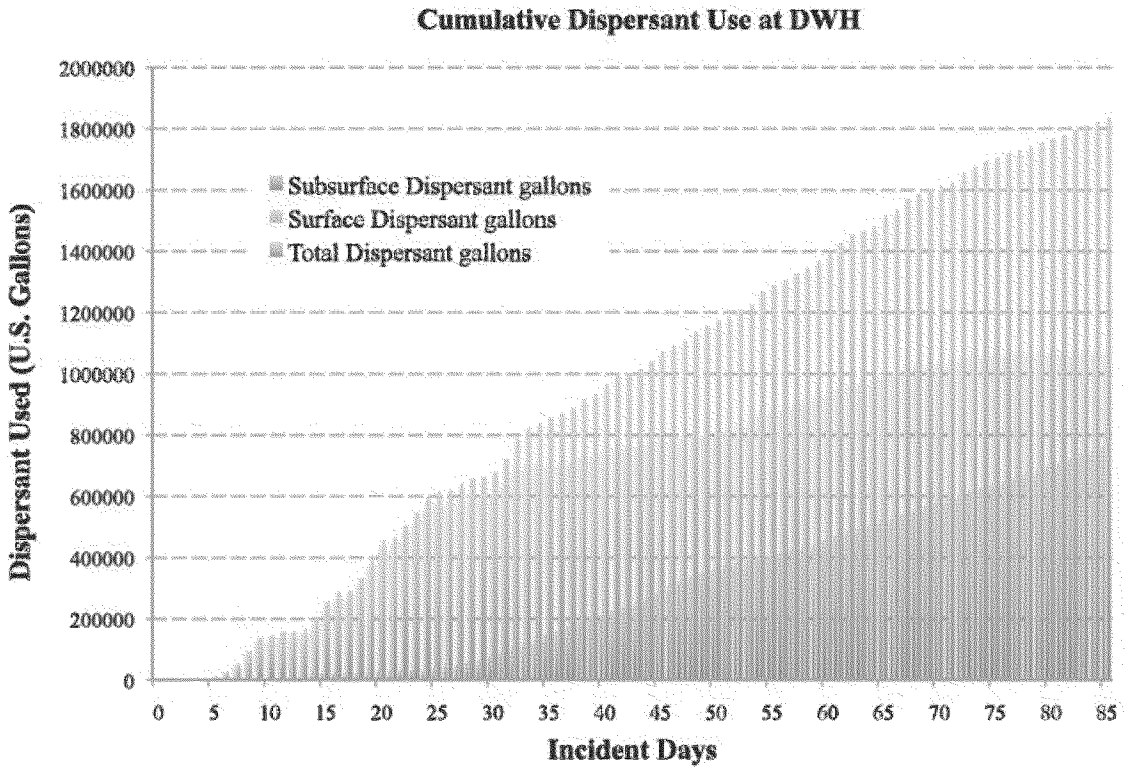

Figure 1. Cumulative surface and subsurface dispersant use by day of spill response (Federal Interagency Solutions Group, 2010).

Dispersant Transport and Fate following the DWH Spill

Corexit 9500 and 9527 were the main dispersants used in response to the BP *-Deepwater Horizon* oil spill. Detailed formulation and ingredient information on COREXIT dispersant products were released to the US EPA for its Gulf monitoring and environmental risk assessment program (Nalco, 2011). The surfactants in these products are similar, including several non-ionic compounds-sorbitan monooleate (Span 80), polyethoxylated sorbitan monooleate (Tween 80), and polyethoxylated sorbitan trioleate (Tween 85)—and the anionic surfactant diethylhexyl sulfosuccinate (DOSS) (Nalco, 2011), but the relative proportions of these compounds may d iffer somewhat between products (Kujawinski et al., 2011) . The biodegradability of chemic al constituents was a criterion in the selection of their formulation by the manufacturer to minimize potential for risks to the environment or public health associated with its use.

As the dispersants could be br oken down rapidly in seawater; the individu al chemical constituents 2-butoxyethanol, dipropylene glycol n-butyl ether (DPnB), propylene glycol, and dioctyl sodium sulfosuccinate (DOSS) were selected for analysis of water samples to determine the expanse of the Deepwater Horizon dispersed oil and Corexit (Operational Science Advisory Team , 2010). These compounds represent major constituents of Corexit, including those with known toxicology data, a those with newly established analytical methods.

Benchmark levels for the individual compounds are established to explain the relevance of measured concentrations (concentrations above benchmark levels are levels of concern.") The benchmarks were based on available biologi data were set at a conservative level to be protective. Aquatic also recognized that the target compounds were also used in other commercial products besides Corexit. Thus, the other sources of the individual chemicals were to be consi the benchmark values were exceeded.

Except for offshore water column samples (79% positive), the dispersant indicators were observed in a small fraction (< 10%) of the samples that were tested. DPnB was one of the most commonly observed dispersant indicator compounds (57 of the 60 positive water samples), but its concentration never exceeded 3 µg/L (Table 1).

Table 1. Samples from the Gulf of Mexico analyzed for the presence of Corexit dispersant indicators; data from the Operational Science Advisory Team (2010).

Zone	Profile	Undetected	Below Benchmark
Nearshore	water column	4790	60
	Sediment	406	6
Offshore	water column	251	199
	Sediment	242	1
Deep Water	water column	3761	353
	Sediment	119	1

* no exceedence of EPA's dispersant benchmarks were observed.

Propylene glycol was the only dispersant indicator detected in the nearshore sediments. Concentrations of DPnB decreased over time (Figure 2), with all values less than 5 µg/L by July 30. The DPnB concentration was highest at the surface and subsurface between 1000 and 1400 m (Figure 3). Deep water concentrations ranged from 0.0170 to 113.4 ìg/L with a mean of 4.3 ìg/L (Operational Science Advisory Team, 2010).

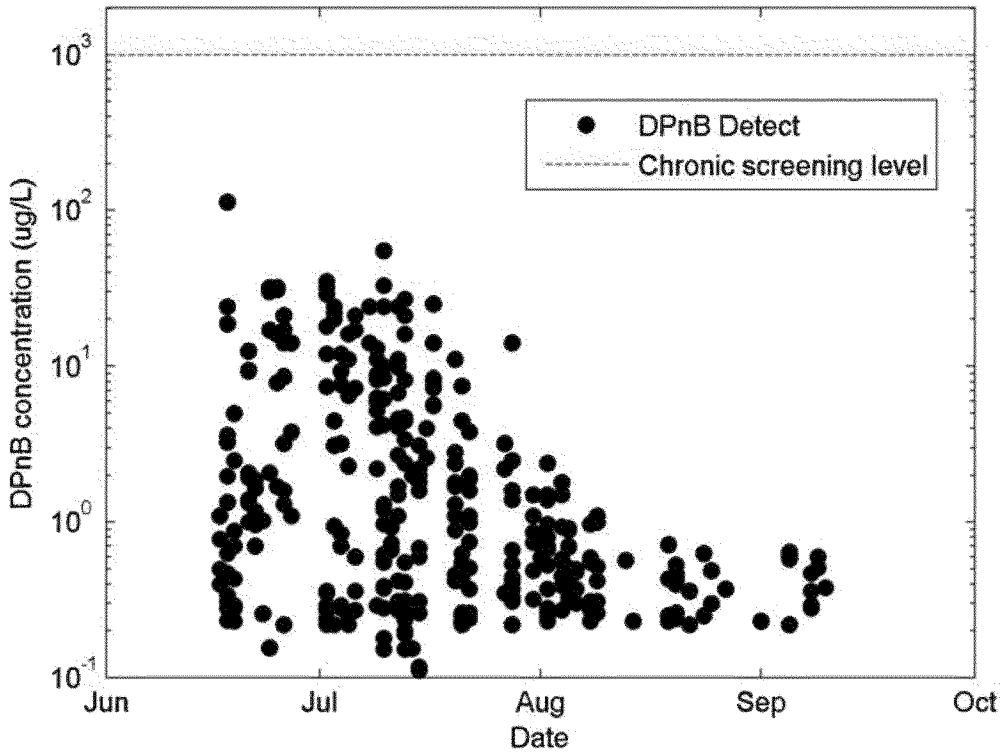

Figure 2. Offshore DPnB concentration over time; the United States Environmental Protection Agency benchmark (chronic screening level) is 1 mg/L (Operational Science Advisory Team, 2010).

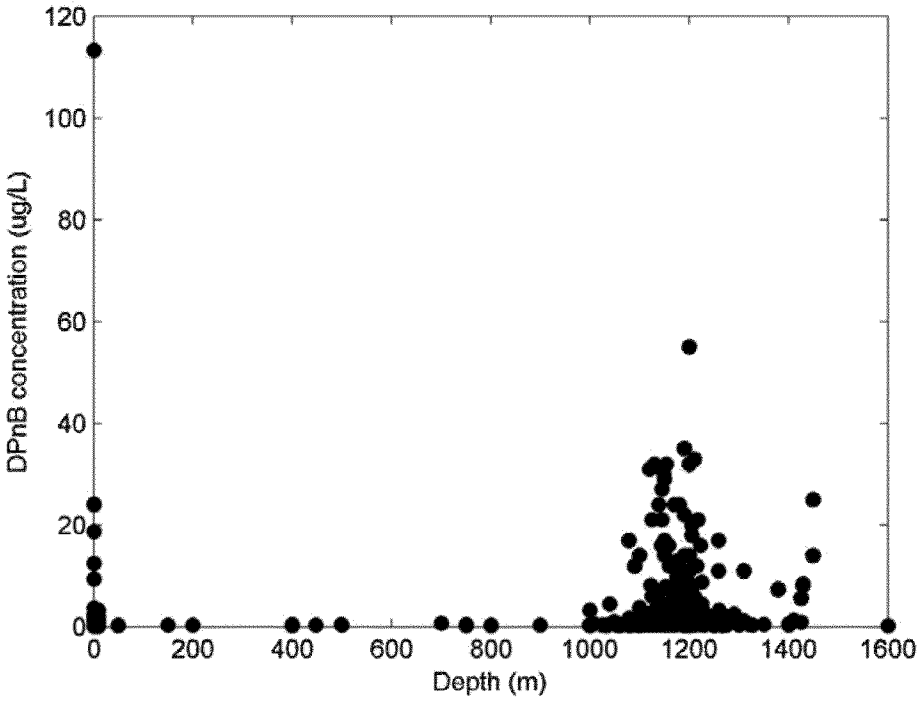

Figure 3. Concentration of DPnB with depth in water samples collected in the deep water zone of the Gulf of Mexico, defined as water depths of greater than 200 m (Operational Science Advisory Team, 2010).

Using advanced liquid chromatography Fournier transform ion cyclotron resonance mass spectrometry, DOSS was detected both during dispersant application, and up to 300 km from the wellhead 64 days after deepwater dispersant injection had ceased (Kujawinski et al., 2011). It was reported that the majority of the DOSS associated with the subsurface injection of Corexit 9500 moved to, and remained in the bottom water layer between 1000 and 1200 m depth rather than rising to the surface (Figure 4). The possibility could not be dismissed that some dissolution with subsequent vertical transport, as well as partitioning with gas or hydrate, might have occurred. The near 1:1 correlation between DOSS and methane (which was found to act as a conservative marker in this situation) and the consistency between their release rates, indicated that DOSS was not biodegraded or otherwise lost near the well head during conditions of active flow, and thus was transported to the 1000 -1200 m layer (Figure 5). The measured concentrations, ranging from 0.4 to 12 µg/L, were remarkably similar to the expected estimated concentrations. Based on the data, Kujawinski et al. (2011) concluded that although biodegradation might have occurred, the most significant factor that caused a decrease in DOSS concentration at depth was dilution. They calculated that biodegradation rates would have had to be approximately ten times the dilution rate in order for it to have been observed (Kujawinski et al., 2011).

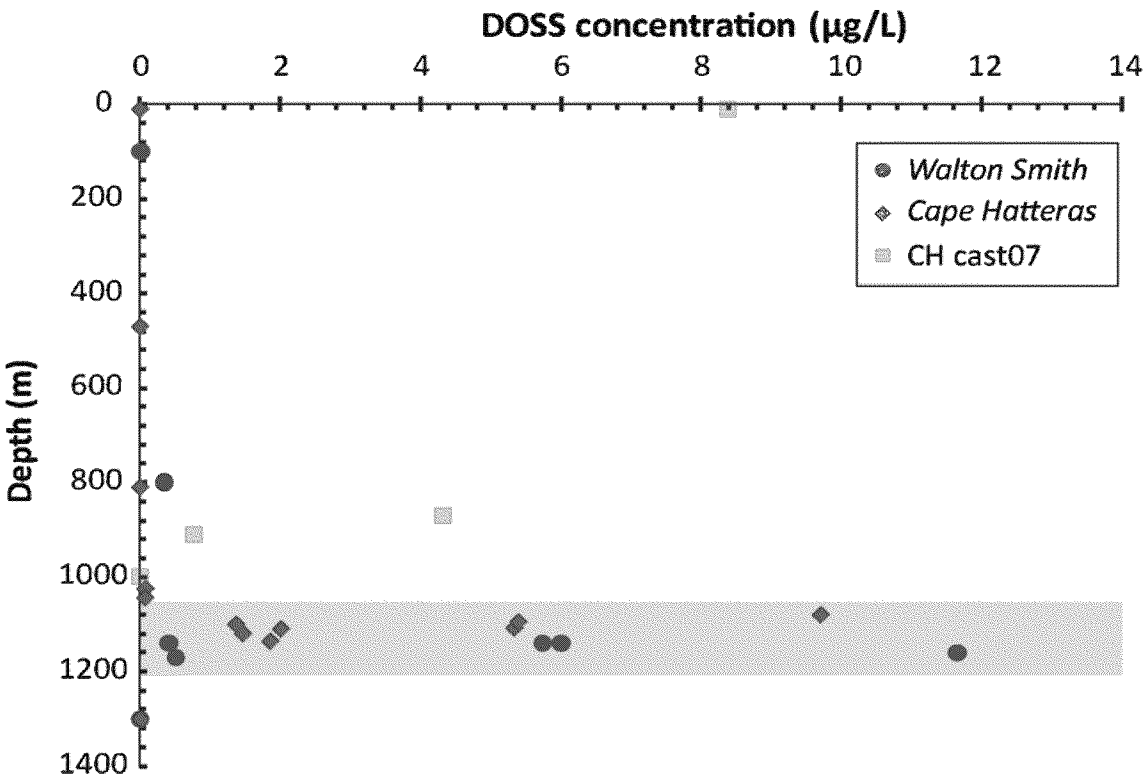

Figure 4. Depth profile of DOSS concentrations falling mainly in the high chromophoric dissolved organic matter zone which included high levels of methane (yellow area), during May and June,

2010, from samples collected by the research vessels *Cape Hatteras* (CH) and *Walton Smith*, with anomalous values from cast07 (Kujawinski et al., 2011).

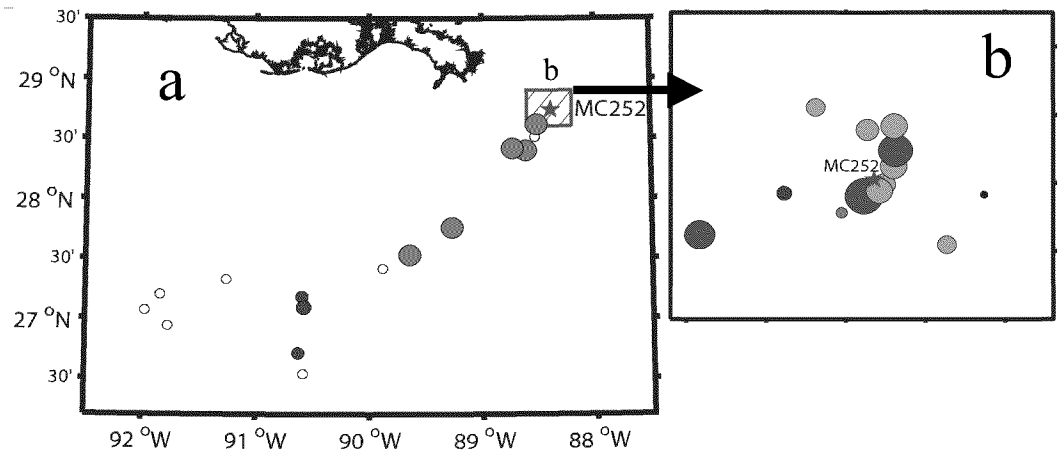

Figure 5. Bird's-eye view of DOSS concentrations at the plume depth of 1000-1200 m in September (a) and May/June (b) with circle size and colour indicative of concentration: white is below detection; blue < 0.01 µg/L; cyan 0.011-0.1 µg/L; green 0.11-1.0 µg/L; yellow 1.0-9.0 µg/L; red > 9.1 µg/L; black indicates the samples were not taken in the plume layer; the star indicates the Deepwater Horizon oil spill site (Kujawinski et al., 2011).

Oil Degradation following the DWH Spill

The recent *DWH* spill has highlighted the importance of natural oil degradation in the recovery of marine ecosystems impacted by crude oil spills. Hazen et al. (2010) reported that the disappearance of residual oil in the Gulf of Mexico from the *DWH* spill was associated microbial degradation processes based on the results of metagenomics. Temperature did not appear to be a major limiting factor as significant rates of oil degradation were observed within the subsea plume of dispersed oil at a depth of 1300 m and temperature below 4 °C. Unlike oil spills occurring at the sea surface, during the *DWH* spill, petroleum hydrocarbons experienced a prolonged, buoyancy -driven ascent through the 1500 m water column (Hazen et al., 2010) . Consequently a unique set of processes affected the released hydrocarbons during their trajectory in the deep sea. Some oil and gas never reached the sea surface, but instead formed hydrocarbon -rich plumes within the cold waters present at about 1100 m depth, supporting an active deep -sea microbial community (Hazen et al., 2010; Valentine et al., 2010) . A combination of integrated chemical, physical and biological processes regulated the transport and fate of hydrocarbons in the deep marine environment. Considering the natural levels of variability and the availability of data at this point of time, it is difficult to disentangle the role of natural processes from the effects of countermeasures such as the use of dispersants.

A considerable amount of research has been focused on the resultant plume of dispersed oil and gas released from the well blow -out that extended southwest from the wellhead between about 1000 and 1200 m below the surface (Camilli et al., 2010; Diercks et al., 2010; Hazen et al., 2010; Kessler et al., 2011; Valentine et al., 2010) . This plume was identified based on fluorescence (Camilli et al., 2010; Diercks et al., 2010; Hazen et al.,

2010), light scattering (Diercks et al., 2010), or the concentrations of specific hydrocarbons (Camilli et al., 2010; Diercks et al., 2010; Kessler et al., 2011; Valentine et al., 2010) and was detectable up to 35 km from the MC252 wellhead (Camilli et al., 2010). The average temperature in the plume was about 5 °C (Camilli et al., 2010; Hazen et al., 2010). Most of these studies also observed a local dissolved oxygen (DO) minimum in the vicinity of the hydrocarbon plume. Camilli and colleagues attributed this minimum to hydrocarbon interference with the *in-situ* DO probes that were used because Winkler titration data did not show oxygen depletion within the plume (Camilli et al., 2010). Other studies, however, showed good agreement between data from the *in-situ* DO probe and Winkler titrations (Kessler et al., 2011; Valentine et al., 2010), suggesting that the rate of aerobic microbial metabolism within the plume was higher than in the surrounding water. Evidence supporting biodegradation of gaseous alkanes (e.g., methane, ethane, propane) (Kessler et al., 2011; Valentine et al., 2010) and higher molecular weight normal alkanes (Kessler et al., 2011) was obtained based on compositional changes that reflected preferential utilization of specific compounds and (for ethane and propane) changes in °C (Valentine et al., 2010). One study estimated that about 70% of the oxygen depletion that was observed within the plume was due to microbial metabolism of ethane and propane (Valentine et al., 2010). Microbial degradation of other hydrocarbons, including butane and longer chain alkanes, was responsible for the additional oxygen depletion. Hazen and colleagues estimated half-lives between about 1.2 and 6.1 days for higher molecular weight normal alkanes based on *in-situ* and microcosm data (Comber et al., 2003). Because their biodegradation rate model did not include biomass concentration, however, and the *in-situ* half-lives did not consider dilution as a factor contributing to the observed changes in compound concentration, the similarity among the observed half-lives should not be over interpreted.

Flocs from samples collected within the plume between May 25 to June 2 were rich in microbes, oil, and oil degradation products, and bacterial counts were elevated within the plume (Hazen et al., 2010). The abundance of genes involved in hydrocarbon degradation were significantly enhanced ($p < 0.05$ or 0.01) in plume samples, and there was a positive correlation with the concentration of low molecular weight components in the oil, suggesting that the composition of the bacterial community changed in response to the presence of oil (Hazen et al., 2010). Cloning and sequencing of 16S rRNA genes showed that the relative abundance of 16 taxa of ã-Proteobacteria, including representatives of known psychrophilic and psychrotolerant hydrocarbon degraders, were higher inside the plume. The most abundant species in samples from within the plume (comprising about 90% of sequences) belonged to a single operational taxonomic unit that was closely related to *Oceanospirillales* (Hazen et al., 2010). Note that observations of samples collected in the same area by another research group about two weeks later, while oil was still being released from the wellhead, did not confirm high levels of *Oceanospirillaceae*, but the samples were dominated by other putative hydrocarbon degraders, especially relatives of *Colwellia* and *Cycloclasticus*, which were thought to be growing on propane, ethane, and butane (Valentine et al., 2010).

Recently, Lu et al. (2011) showed that the microbial community functional composition and structure were dramatically altered in the deep-sea from the Deepwater Horizon spill.

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A variety of metabolic genes involved in aerobic and anaerobic hydrocarbon degradation were highly enriched in the plume than outside the plume. Various other microbial functional genes that are associated w ith carbon, nitrogen, phosphorous, sulfur, and iron cycling, metal resistance, and bacteri ophage replication were also enriched in the plume. The authors suggest that the indigenous marine microbial communities could have a significant role in biodegradation of oil spills in deepwater.

In summary, the size and composition of the Gulf of Mexico microbial community was altered as microbes responded to the presence of oil. Bacterial cell densities were significantly higher in the plume, 10^5 cells mL^{-1}, as com pared to numbers outside the plume, which was 10^3 cells mL^{-1} (Atlas and Hazen, 2011). As the community responded, hydrocarbon degraders dominated, resulting in reduced community diversity. DNA surveys for bacterial 16S rRNA genes from samples collected in June revealed dominance of *Cycloclasticus* and *Colwellia*, likely degrading propane and ethane preferentially (Kessler et al., 2011; Valentine et al., 2010). Sixteen taxa of the γ-proteobacteria dominated by the order *Oceanospirillales* occurred in high numbers and dominated the co mmunity in plume samples collected in the same time frame (Hazen et al., 2010). Among these were *Oliespira antarctica, Thalassolituus oleivorans,* and *Oliphilus messinensis*, bacteria known to degrade hydrocarbons and tolerate low temperatures that occur in the deep sea. Sam ples collected later (September) indicated a shift away from these hydrocarbon degraders to methanotrophs, including *Methylococcaceae*, *Methylophaga*, and *Methylophilaceae*. The enhanced abundance of methanotrophs and bacteria containing the particulate methane monooxygenase gene (pmoA) indicated that methane was consumed later in the spill sequence by a different bacterial assemblage (Kessler et al., 2010).

Propane and ethane were degraded relatively rapidly and likely before alkanes >5 carbons in length (Va lentine et al., 2010). The occurrence of natural seeps in the area of the spill may have supported the development and persistence of microbial communities capable of degrading hydrocarbons. Dissolved propane and ethane may promote rapid hydrocarbon degradation and low diversity communities that can degrade other hydrocarbons as the nature of remaining hydrocarbons changes. Hazen et al. (2010) estimated biodegradation rates for hydrocarbons in the plume based on observed concentrations of C13 -C26 alkanes fr om samples collected near the MC252 plume and from laboratory degradation studies at 5 °C. Based on these observations, degradation of alkanes was estimated to be 1.2–6.1 days. Rapid rates of biodegradation may be expected for alkanes, the least recalcitra nt fraction among the complex mixture of compounds that makes up Sweet Louisiana Crude oil. Rapid degradation rates reported for Sweet Louisiana Crude in the region of the MC252 oil spill may be related to its relatively light character, containing a large volatile component and a large fraction of alkanes, both more amenable to degradation than heavier crude oil. Edwards et al . (2011) reported that microbes within the surface slick showed higher rates alkaline phosphate activity, indicating enhanced phosphate stress. Microbial respiration and lipase activity rates were also higher with the slick and the degradation of hydrocarbons was fairly rapid and supported the majority of respiration. The authors suggest that the microbial community possessed the potential to respire hydrocarbons at an unprecedented rate, potentially great enough to keep pace with the flux of oil reaching the surface from the Macondo well, and

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the observed differences in microbial respiration and activity between stations within the slick and outside the slick is a testament to the rapid response of the microbes in surface waters of the Gulf of Mexico to oil from the Deepwater Horizon spill.

The composition of the oil fraction from MC252 estimated by Reddy et al. (2011) indicated 74% saturated hydrocarbons, 16% aromatic hydrocarbons and 10% polar hydrocarbons. Gas chromatographic analysis for several monoaromatic compounds indicated benzene, toluene, ethylbenzene and total xylenes (BTEX) concentrations exceeding 50 $\mu g\ L^{-1}$ within the plume in June 2010 (Camilli et al., 2010). Estimates for hydrocarbon degradation in the plume range from 2 –7 $\mu g\ L^{-1} d^{-1}$, which translates to an estimated half-life of about 1 month for petroleum hydrocarbons (Reddy et al., 2011). Methane was estimated to take longer to degrade. Kessler et al. (2011) estimated the oxidative lifetime of methane resulting from the spill to be 120 days.

Lessons Learned from Deepwater Horizon Spill Response and Future Challenges

About 2.1 million gallons of dispersant were used during the *Deepwater Horizon* spill response, and about 8% of the oil that was released is thought to have been chemically dispersed (Lubchenco et al., 2010). Based on current knowledge, it is believed that most of the chemically dispersed oil, including the MC252-derived hydrocarbons in the deep plume, may have been biodegraded within the environment following its release. Indirect evidence consistent with the expected biodegradation included identification of genes known to be involved in hydrocarbon biodegradation, enrichment of 16S rRNA sequences related to known hydrocarbon degraders, and depletion of dissolved oxygen within the deep dispersed oil plume. In light of the large uncertainties associated with measurements of hydrocarbon fate following accidental spills, fate and transport modeling may offer the best means for evaluating the relative impacts and benefits of chemical dispersion in spill response.

Due to the low concentrations of dispersant following its application in the Gulf of Mexico, as the result of physical dispersion and dilution processes, as well as the intrinsic levels of variability within an open-ocean environment, it is impossible to extract concrete evidence to support the hypothesis that the dispersant surfactants biodegraded rapidly in subsurface waters. Additional research is warranted to enhance better and more quantitative understanding of the fate of dispersants and chemically dispersed oil, particularly in subsurface. In terms of potential environmental risk, it is important to note that all of the surfactants used in Corexit 9500 and Corexit 9527 are known to be at least partially biodegradable under appropriate conditions. Indeed, dispersants themselves can enhance the initial rate of petroleum hydrocarbon degradation by being the first substrate utilized by the hydrocarbon degrading bacteria to grow and colonize dispersed oil droplets (Varadaraj et al., 1995).

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Lab tests on the biodegradation of chemically dispersed oil should consider the rapid dilution that occurs at sea

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abstract

Most crude oils spread on open water to an average thickness as low as 0.1 mm. The application of dispersants enhances the transport of oil as small droplets into the water column, and when combined with the turbulence of 1 m waves will quickly entrain oil into the top 1 m of the water column, where it rapidly dilutes to concentrations less than 100 ppm. In less than 24 h, the dispersed oil is expected to mix into the top 10 m of the water column and be diluted to concentrations well below 10 ppm, with dilution continuing as time proceeds. Over the multiple weeks that biodegradation takes place, dispersed oil concentrations are expected to be below 1 ppm. Measurements from spills and wave basin studies support these calculations. Published laboratory studies focused on the quantification of contaminant biodegradation rates have used concentrations orders of magnitude greater than this, as it was necessary to ensure the concentrations of hydrocarbons and other chemicals were higher than the detection limits of chemical analysis. However, current analytical methods can quantify individual alkanes and PAHs (and their alkyl homologues) at ppb and ppm levels. To simulate marine biodegradation of dispersed oil at dilute concentrations commonly encountered in the field, laboratory studies should be conducted at similarly low hydrocarbon concentrations.

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1. Introduction

The primary goal of any oil spill response operation is to minimize harm to people and the environment. Complete containment and removal of oil from the environment is an expectation that is improbable or impossible for large offshore spills due to physical limitations of mechanical recovery systems. In fact, mechanical recovery operations in the offshore only collect a small fraction of oil even under ideal circumstances (ITOPF, 2010). The extensive mechanical recovery operations during the Deepwater Horizon response were estimated to have recovered only 3% of the oil (NOAA, 2010).

Alternative response tools, such as oil spill dispersants, were developed because of the known limitations of mechanical recovery for large offshore spills. Dispersants, applied at the surface or subsea, allow rapid atomization of large volumes of oil, and thereby facilitate the removal of oil from the environment through biodegradation. Dispersants break a surface slick into micron-sized droplets that are transported into the water column and rapidly diluted. The small oil droplets are now a readily accessible food source for oil degrading bacteria. All marine environments contain petroleum-degrading bacteria because of the abundance of natural oil seeps (Prince et al., 2010).

The rapid dilution that occurs in the open oceans allows bacteria to aerobically biodegrade dispersed oil without exhausting natural levels of biologically available nutrients or oxygen. Laboratory studies have shown that oil degrading microbes colonize dispersed oil droplets within a few days (MacNaughton et al., 2003), and the composition of some dispersants even enhances biodegradation by serving as an initial food source for bacterial growth (Lee et al., 1985; Varadaraj et al., 1995). Fig. 1 illustrates the biodegradation process after applying surface and subsea dispersants.

Measurements made in the Gulf of Mexico indicate that biodegradation is rapid in marine environments (Hazen et al., 2010; Valentine et al., 2012), but there is a significant amount of seemingly contradictory evidence on the biodegradation of dispersed oil in the laboratory. We propose that many of the contradictions are likely the result of study designs that are unrepresentative of the field conditions encountered in the Gulf of Mexico and most oil spills at sea, or limitations in lab-based test methods. This paper

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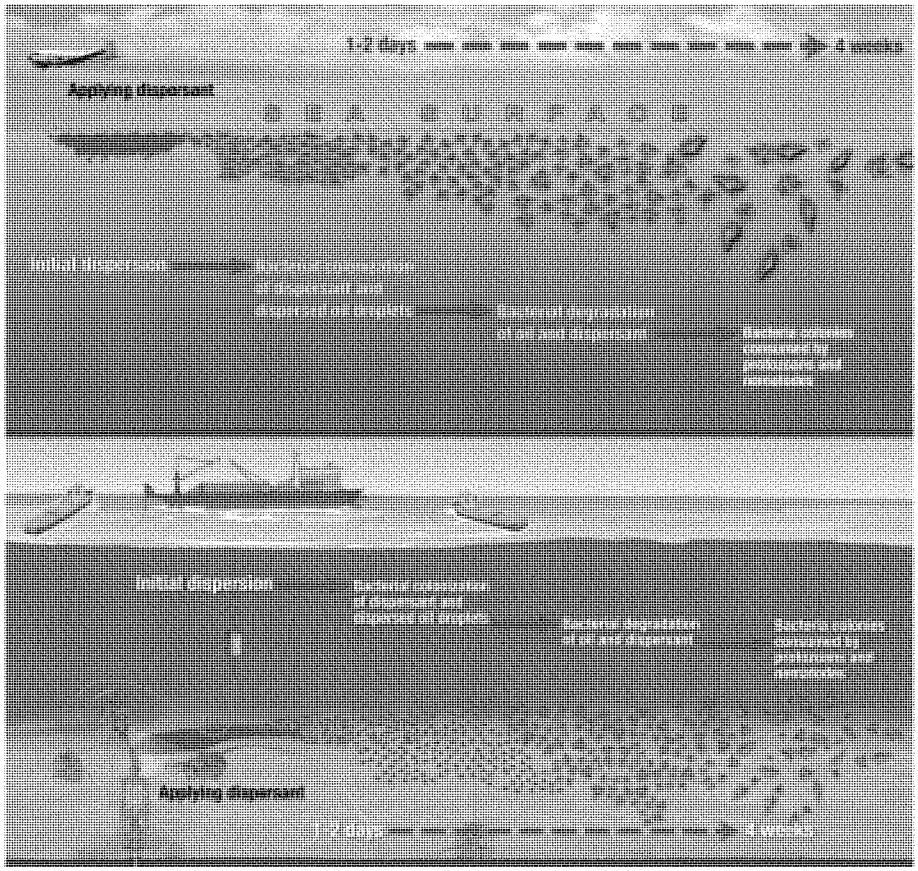

Fig. 1. Diagram illustrating the biodegradation process that begins when dispersants are applied to surface slicks (top) and to a deepwater release (bottom).

describes the important characteristics of plume dilution and dispersion stability that should be accounted for during microcosm studies of dispersed oil fate and effects. We provide evidence from field and wave basin studies to show the speed of dispersed oil dilution and the stability of effective dispersion.

2. Background

Conducting representative biodegradation studies on dispersed oil in a closed microcosm has at least two important challenges that need to be considered. The first challenge is to determine what are the low dispersed oil concentrations representative of field conditions that a researcher wants to investigate, and how to conduct tests at these concentrations. Low-viscosity oil is expected to have an average thickness of 0.1 mm on the sea surface (based on Lehr et al., 1984). Applying dispersants to a slick in 1 m waves causes mixing of dispersed oil into the top 1–1.5 m of the water column (Delvigne and Sweeney, 1988). This results in immediate dilution by a factor of 10,000 producing an average oil concentration of 100 ppm (worst case) or less.

Trudel et al. (2009) confirmed the near immediate dilution in wave tank dispersion tests, finding maximum dispersed oil concentrations between 5 and 147 ppm. Dispersion effectiveness for these tests ranged from 85% to 100%. In another wave tank study under continuous flow conditions, Li et al. (2009) found that the concentration of weathered Alaskan North Slope crude oil dispersed with Corexit 9500 declined from 12 ppm to 2 ppm within 60 min (at a depth of 0.75 m 10 m downstream from the dispersant application). Dispersed oil plumes continue to dilute with time, and are estimated to become very dilute in less than a day (French-McCay and Payne, 2001; French-McCay et al., 2007; Cormack and Nichols, 1977; McAuliffe et al., 1980). Dispersed oil plumes are expected to have average oil concentrations well below 10 ppm before biodegradation becomes significant because microbes require more than one day to colonize dispersed oil droplets (MacNaughton et al., 2003). Further, average concentrations are expected to be well below 1 ppm over the weeks to months that it takes for biodegradation to complete.

Unfortunately published biodegradation studies have been conducted at unrealistically high concentrations of dispersed oil in closed microcosms. Prior research either did not account for the rapid dilution that occurs at sea or employed methods that were not sensitive to low concentrations. Dispersed oil concentrations used in biodegradation studies range from: 1400–4500 ppm (Lindstrom and Braddock, 2002), 266 ppm (Swannell and Daniel, 1999), 250 ppm (Davies et al., 2001), 227 ppm (Yoshida et al., 2006), 100–200 ppm (Zahed et al., 2010), and 830 and 83 ppm (Venosa and Holder, 2007). Studying dispersed oil biodegradation at concentrations orders of magnitude above expected at-sea concentrations in closed systems can limit biodegradation rates and total degradation due to the depletion of nutrients. To counteract this effect, some experiments have been done using high initial concentrations of nutrients in the batch system, but this likely leads to an unrepresentative modification of the microbial community. Prince et al. (2013) found that dispersed crude oil at 2.5 ppm was rapidly and extensively biodegraded without the need for added nutrients or bacteria. Other confounding factors also need to be considered. A recent paper by Hamdan and Fulmer (2011) used Corexit 9500 concentrations between 1000 and 10,000 ppm. These dispersant concentrations are three to five orders of magnitude greater than would be expected even immediately after dispersant application

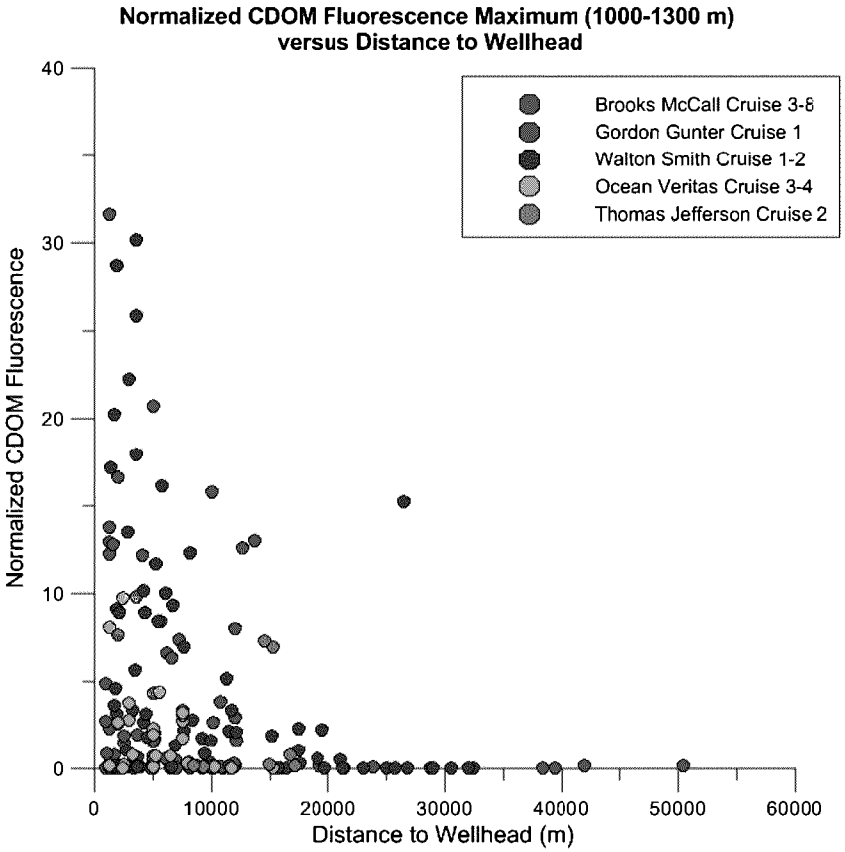

Fig. 2. Mean fluorescence (ppb quinine sulfate dehydrate equivalents, QSDE)) vs. distance from wellhead. Oil concentration (ppm) is derived from the normalized colored dissolved organic matter (CDOM) fluorescence multiplied by a correction factor based on laboratory measurements comparing CDOM fluorescence and MC252 oil with Corexit 9500 at a DOR of 1:25 (calibration factor = 1.2416). Copied from JAG, 2010.

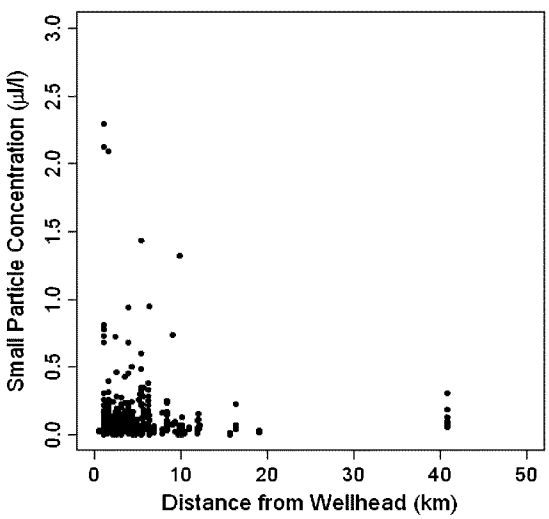

Fig. 3. Small particle concentrations (<70 l m) within the subsurface plume over distance from the wellhead within period of oil release and sub-surface injection of oil dispersants from 8 May to 24 August 2010.

at sea. At these concentrations, it is not surprising that they found that hydrocarbon-degrading bacteria are inhibited by dispersants.

The second challenge with studying dispersed oil biodegradation in a closed system is the difficulty of maintaining a stable dispersion in the laboratory. Dispersed oil in the water column exists as small droplets that neither surface nor sink, and the droplets become so scattered that they cannot coalesce. For biodegradation studies of chemically dispersed oil within the laboratory, mixing is considered essential. If alternative procedures are not used, care must be taken when using centrifugal mixing to minimize the formation of a vortex that concentrates low density oil droplets. It is a challenge to maintain stable oil dispersions in closed systems because natural dilution does not occur, allowing greater droplet-to-droplet contact and coalescence.

Lewis (2004) estimated that the droplet diameter required to keep dispersed oil from resurfacing was <100 l m. The exact diameter depends on the oil density and light oils require a diameter <70 l m to keep droplets from resurfacing in moderate seas. Wave tank tests by Li et al. (2008, 2009) using light-medium oils found dispersed oil droplets with median diameters <50 l m. Lunel (1993, 1994a,b, 1995) reported mean droplet diameters between 15 and 25 l m during field measurements of dispersant-treated oil slicks at sea. Thus, to simulate the dispersion of oil at sea, biodegradation studies require formation of a stable dispersion containing droplets no greater than 70–100 l m and enough mixing energy to keep droplets from resurfacing during an experiment.

3. Field data from the Deepwater Horizon incident

During the Deepwater Horizon spill, oil and gas were discharged from the wellhead at 1544 m below the sea surface for 87 days. A total of 0.78 million gallons of the chemical dispersant Corexit 9500A (Nalco) were applied directly at the wellhead (NOAA, 2010). Turbulent energy from the release of gas and oil from the well resulted in the formation of a subsurface plume of dispersed oil droplets that was observed between 1000 and 1400 m depth;

it began near the release area and trended primarily southwest consistent with water movement along isobaths.

Despite a sustained period of oil release (thought to be 8400 m^3/day) with concurrent additions of dispersant over a prolonged period of time, the field data showed a rapid decrease in the concentration of the plume with distance due to physical dilution processes and the biodegradation of oil (Fig. 2). The highest recorded mean oil concentration measured at 1 km from the source was 10 ppm (R/V Brooks McCall; 30 May 2010), while P 10 km the highest mean oil concentration was 3 ppm, with most concentrations in the ppb range (R/V Gordon Gunter; 2 June 2010) (JAG, 2010).

Samples of water recovered from within the plume during the same R/V Brooks McCall surveys (191 locations) showed that >80% of the subsurface particles were <70 l m (with ffi20 l m median diameter) (Fig. 3). These sizes are in good agreement with previous observations of chemically dispersed oil at sea (Lunel, 1993, 1994a,b, 1995) and in controlled experimental wave tank studies (Li et al., 2008, 2009).

The stimulation of deep-sea indigenous bacteria with the capacity to degrade oil during the Deepwater Horizon spill was clearly demonstrated by Hazen et al. (2010) and Valentine et al. (2012) even though the temperature was 4 fC. Both studies highlight the rapid and prolonged bacterial bloom and subsequent increased biodegradation rates in response to the elevated hydrocarbon presence at low overall oil concentrations.

4. Summary and conclusions

Chemical oil dispersants can rapidly break up surface slicks by diluting the oil into the water column to very low concentrations. This has been clearly demonstrated by wave tank studies and further corroborated by the direct measurements taken during the Deepwater Horizon oil spill. Although recent research cites concentrations almost three orders of magnitude greater, oil concentrations in the low ppm range should be duplicated in the laboratory for oil degradation studies, since it is at these concentrations that the dispersed oil is amenable to biodegradation by microbes, as they will not suffer toxic effects from the dispersant or oil. This situation is a better representation of the environment in field situations in which microbial oil degradation occurs.

It should be noted that up to 90% of indigenous bacteria in marine systems may not survive in culture (Amman et al., 1995); therefore the bioremediation potential of deep-sea microorganisms may not have been accounted for in previous studies. We are now capable of observing changes in the function of whole populations rather than the activity of isolates in culture.

Future laboratory studies that focus on the biodegradation, fate and effects of dispersed oil should attempt to account for the rapid dilution and stability of low concentrations of dispersed oil similar to those found in plumes in the field. When these environmental conditions are used, rapid and significant biodegradation of dispersed oil is expected.

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Short Communication

FATE OF OIL DISPERSANTS IN AQUATIC ENVIRONMENT

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ABSTRACT

Chemical oil dispersants have been used throughout most of the world to combat oil spills. However, their fate in aquatic environment remains uncertain. This study was conducted to investigate the persistence of five oil dispersants in the aquatic environment. The results indicate that petroleum utilizing bacteria possess high potential for the biodegradation of oil dispersants. The order of biodegradability for the five oil dispersants was as follows: Magnus 101 > BP1100X > BP1100 > Linco No. 4 > Corexit 8666. From the results of this study and a review of the literature data, it can be concluded that treatment of oil spills with chemical dispersants is unlikely to cause any build-up of organic contaminants in the aquatic environment.

INTRODUCTION

Accidential spillage of crude oil or petroleum products appears to be an inevitable consequence during the processes of extracting, manufacturing and transportation of petroleum hydrocarbons (Atlas, 1981). Unfortunately, most of these spillages occur in aquatic environments because of the substantial involvement of water transportation for such commodities as well as with the increased oil drilling activities in the continental shelf. Oil spills are, probably one of the major sources of organic contaminants for the aquatic environment. The ecological consequences of each oil spill incident varies, depending on the magnitude of the spill, the chemical composition of the oil and the nature of the contaminated ecosystem.

Various physical and chemical techniques have been developed for cleaning oil spills. The physical approach is intended to confine or remove the spilt oil from the surface water. However, the current state-of-the-art for containment and removal of oil spills from offshore waters has distinct limitations (McCarthy et al., 1978). For instance, containment booms only can be applied to seas with waves not exceeding two feet or currents less

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than two knots. Other available physical options such as burning, sinking, gelling, or the use of sorbents are even less desirable, being either environmentally unacceptable or technically unfeasible. The chemical control of oil spills mainly involves the use of dispersants to break up oil slicks and thus disperse the oil in the water column, which, otherwise, may threaten to pollute shoreline areas (Mulkins-Phillips and Stewart, 1974). Other advantages of using dispersants are the removal of a potential fire hazard, facilitation of evaporation, and enhancement of biodegradation processes (Slade, 1982). Consequently, chemical oil dispersants have been used throughout most of the world to combat oil spills (Albers and Gay, 1982). Much knowledge has been gathered regarding the toxicity of oil dispersants towards birds (Albers and Gay, 1982), fish (Slade, 1982), and algae (Heldal et al., 1978). There has been, in general, a lack of information concerning the persistence of oil dispersant in the aquatic environment. This study was conducted to assess the fate of oil dispersants in the aquatic ecosystem using an oil degrading bacterium.

MATERIALS AND METHODS

Medium

The basal mineral medium used for growing the crude oil degrading bacterium had the following ingredients ($g\,l^{-1}$): K_2HPO_4, 0.66; KH_2PO_4, 0.41; $MgCl_2 \cdot 6H_2O$, 0.10; $FeCl_2 \cdot 4H_2O$, 0.05; $MnCl_2 \cdot 4H_2O$, 0.002; and $(NH_4)_2SO_4$, 0.50. The final pH of the medium was 6.9, and it was sterilized at 121°C for 15 min. The crude oil (Norman Wells) was sterilized separately under the same conditions and was added aseptically to the medium at a concentration of $4\,ml\,l^{-1}$.

Culture

The crude oil-degrading bacterium, CM01, used in this study was originally isolated from a local refinery soil (Liu and Dutka, 1972). The culture was grown in a 2-l Bellco spinner flask containing 1 l of basal mineral medium and 4 ml of crude oil. The flask was incubated on a magnetic stirrer with agitation at room temperature (21°C). Since hydrocarbon-utilizing bacteria can only grow at the oil—water interface (Traxler and Bhattacharya, 1978), the magnetic spindle inside the flask was set at the fast spin setting, (300—400 rpm) to increase the area of such interfaces. With 10% inoculum, an incubation time of 18—20 h was adequate to harvest the cells for use in manometric experiments.

Manometric Studies

The cells were harvested by centrifugation at 10,000 × *g* for 20 min at 4°C, followed by two washes with 0.02 *M* phosphate buffer at pH 7.0. The resulting packed cells were resuspended in cold 0.05 *M* phosphate buffer (pH 7.0) to give a cell concentration of approximately 20 mg dry weight

ml^{-1}. The overall oxygen consumption as determined in a Gilson differential respirometer was taken as a measure of the biodegradation potential ($Q_{O_2} = \mu l\, O_2\, h^{-1}\, mg^{-1}$ cell dry weight) of culture CM01 against oil dispersants. The composition of the assaying preparation, unless otherwise stated, consisted of 1 ml of cell suspension (approx. 20 mg), 1 ml of 0.05 *M* phosphate buffer, 0.8—0.9 ml of distilled water, 100—200 μl substrate, and 0.2 ml of 20% KOH (in the center well of the Warburg flask for CO_2 absorption). Total volume of the reaction mixture was 3.2 ml. The experiments were performed at 20°C with a steady shaking rate of 105 strokes min^{-1}.

Dry weight

Thirty ml of the culture broth were centrifuged at 15,000 × *g* for 20 min, followed by two washes in distilled water. The cell pellet was taken up in 5 ml of distilled water and dried for 20 h at 105°C.

RESULTS AND DISCUSSIONS

The bacterial culture, CM01, was selected for this study from 7 isolates, on the bases of its rapid growth on crude oil. The culture exhibited good potential for the biodegradation of the oil dispersant, BP1100X (Fig. 1). In these experiments, various amounts of BP1100X were added to 250-ml erlenmeyer flasks, containing 100 ml of basal mineral medium, and 1 ml of inoculum. Dry weight determinations were followed at various time intervals (10, 20, and 24 h). The CM01 culture was found to be capable of growing rapidly in different BP1100X concentrations (100—10,000 ppm) as sole carbon and energy source without acclimatization. At BP1100X concentrations below 3 ml l^{-1}, there was a linear relation between cell yield (dry

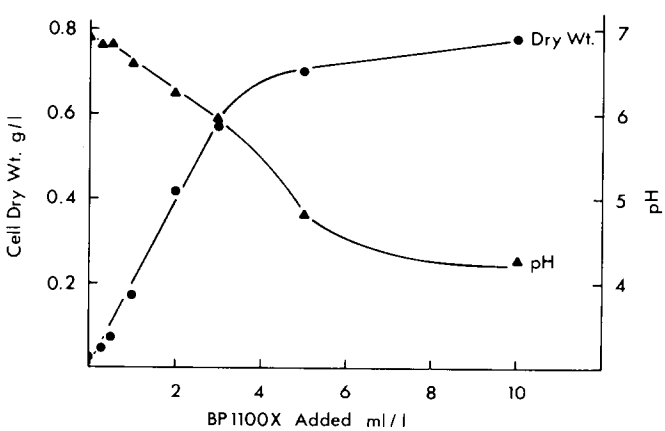

Fig. 1. Effect of BP1100X concentrations on cell yield and final medium pH.

weight) and substrate utilization with a rate of 0.218 ml BP1100X h^{-1} g^{-1} cell dry weight. The cell yield, however, leveled off at higher BP1100X concentrations (4—10 ml l^{-1}), possibily due to the lowering of the medium pH by the culture activity. For instance, an increase of BP1100X concentration in the growth medium from 3 ml l^{-1} to 5 ml l^{-1}, was found to cause a corresponding decrease of the medium pH from 6.0 to 4.8 (Fig. 1).

The ability of the culture CM01 to degrade the oil dispersant BP1100X is further supported by the manometric experiments. In these studies, various amounts of BP1100X (1, 2, 5, 25, 50, 100 and 200 μl) were subjected to oxidation by CM01 in the Warburg flasks. The results presented in Fig. 2 indicate a good correlation between BP1100X concentration and total oxygen consumption. Since BP1100X was the only substrate in the Warburg reaction mixture, the amount of oxygen uptake by CM01 would indicate that BP1100X was utilized by the culture for respiration. Between the BP1100X concentration ranges of 0 to 25 μl $flask^{-1}$ (0—8333 ppm), the amount of oxygen used by the culture CM01 was a direct function of the BP1100X concentrations. It should be noted that with all concentrations of BP1100X used in these experiments, there was no lag period for oxygen uptake, suggesting that the culture CM01 was capable of immediately oxidizing the oil dispersant BP1100X at all concentrations used.

Various oil dispersants have been used for the treatment of oil spills (McCarthy et al., 1978; Albers and Gay, 1982). It would be advisable to determine the order of their persistence in aquatic environment. Thus, high concentrations (33,332 ppm) of five oil dispersants (Magnus 101, BP1100X, BP1100, Linco No. 4, Corexit 8666) and on crude oil (Norman Wells) were

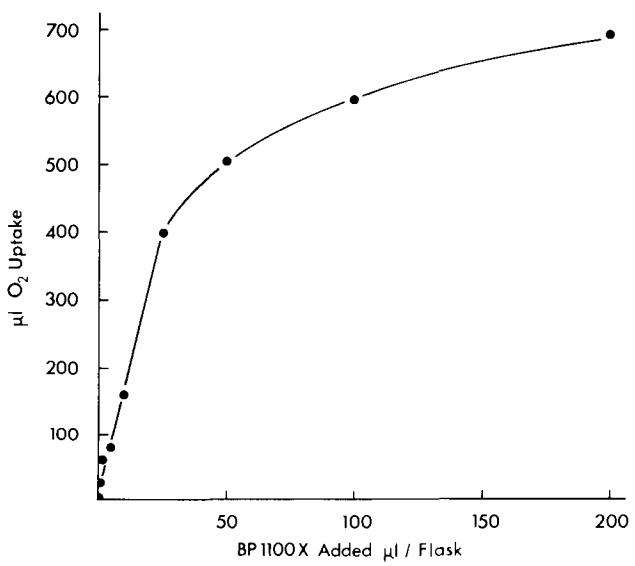

Fig. 2. Total oxygen consumption (60 min) as a function of BP1100X concentrations in the Warburg flasks.

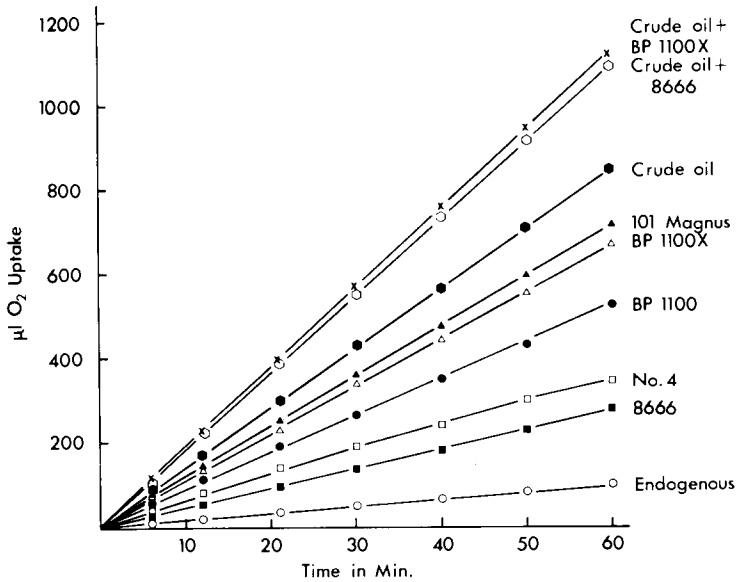

Fig. 3. Oxidation of various oil dispersants by culture CM01.

subjected to culture CM01 oxidation in the Warburg flasks (Fig. 3). Oil dispersant concentrations used in these experiments were about 2.7 times higher than those employed under field situations (Mulkins-Phillips and Stewart, 1974). The immediate response in oxygen uptake (Fig. 3) by the culture CM01, upon addition of the dispersants, suggests that the hydrocarbon utilizing bacteria possess an inherent potential to degrade oil dispersants, i.e., playing an important role in the removal of dispersant from aquatic environment.

The order of biodegradability for the five oil dispersants was determined in terms of Q_{O_2}: Magnus 101 (Q_{O_2} = 34.0), BP1100X (Q_{O_2} = 31.1), BP1100 (Q_{O_2} = 24.6), Linco No. 4 (Q_{O_2} = 16.3) and Corexit 8666 (Q_{O_2} = 13.5). The overall lower Q_{O_2} values (13.5—34.0) for these oil dispersants compared to the crude oil Q_{O_2} (40.0) is probably more desirable in that the dispersants would not be preferentially utilized as carbon sources over the oil by aquatic microorganisms. Petroleum utilizing microorganisms are known to be widely distributed in aquatic environment (Atlas, 1981) and the results in this study demonstrate the susceptibility of oil dispersants to immediate biodegradation by such microorganisms. Thus, it appears that treatment of oil spills with dispersants is not likely to have any significant impact on the build-up of organic contaminants in aquatic environment.

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RESEARCH

Biodegradation of Dispersed Forties Crude and Alaskan North Slope Oils in Microcosms Under Simulated Marine Conditions

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For oil spills in the open sea, operational experience has found that conventional response techniques, such as mechanical recovery, tend to remove only a small fraction of oil during major spills, a recent exception being the Mississippi River spill in Louisiana [Spill Sci. Technol. Bull. 7 (2002) 155]. By contrast, the use of dispersants can enable significant fractions of oil to be removed from the sea surface by dispersing the oil into the water column. It is thought that once dispersed the oil can biodegrade in the water column, although there is little information on the mechanism and rate of biodegradation. Two studies were undertaken on dispersion, microbial colonisation and biodegradation of Forties crude and Alaskan North Slope (ANS) oils under simulated marine conditions. The study using the Forties crude lasted 27 days and was carried out in conditions simulating estuarine and coastal conditions in waters around the UK (15 C and in the presence of nutrients, 1 mg $N\text{-}NO_3/l$), while the ANS study simulated low temperature conditions typical of Prince William Sound (8 C) and took place over 35 days. The results of both studies demonstrated microbial colonisation of oil droplets after 4 days, and the formation of neutrally buoyant clusters consisting of oil, bacteria, protozoa and nematodes. By day 16, the size of the clusters increased and they sank to the bottom of the microcosms, presumably because of a decrease in buoyancy due to oil biodegradation, however biodegradation of n-alkanes was confirmed only in the Forties study. No colonisation or biodegradation of oil was noted in the controls in which biological action was inhibited. Oil degrading bacteria proliferated in all biologically active microcosms. Without dispersant, the onset of colonisation was delayed, although microbial growth rates and population size in ANS were greater than observed with the Forties. This difference reflected the greater droplet number seen with ANS at 8 C than with Forties crude at 15 C. Although these studies differed by more than one variable, complicating comparison, the findings suggest that dispersion (natural or chemical) changes the impact of the oil on the marine environment, potentially having important implications for management of oil spills in relation to the policy of dispersant use in an oil spill event.
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Introduction

Operational experience following major oil spills has shown that the use of dispersants can enable significant amounts of oil to be removed from the sea surface by dispersing the oil into the water column

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(Green et al., 1982, Lunel et al., 1995). In comparison, conventional response techniques such as mechanical recovery, remove only a small fraction of oil. It is well known that bacteria are able to degrade oil dispersed in the water column (Floodgate, 1984; Bartha & Atlas, 1987). Oil dispersion is thought to stimulate the rate of hydrocarbon degradation by increasing the surface area of the oil available for microbial attack (Singer & Flaherty, 1984; Leahy & Colwell, 1990).

While a substantial amount ofresearch has been conducted into the impact ofchemical dispersants on the fate of dispersed oil, results have often been conflicting. Some workers have proposed that dispersants had little effect on oil biodegradation, while others suggest a positive effect and some note a negative effect (Robichauz & Myrick, 1972; Mulkins-Phillips & Stewart, 1974; Traxler & Bhattacharya, 1979; Foght & Westlake, 1982; Lee et al., 1985; Literathy et al., 1989). It has been suggested that dispersants increase oil biodegradation by increasing the surface area for microbial attack, and encouraging migration of the droplets through the water column making oxygen and nutrients more readily available (Mulyono et al., 1994). However, some dispersants were also found to have a toxic effect on microbial processes retarding the rate of oil decomposition (Mulyono et al., 1994; Varadaraj et al., 1995). Varadaraj et al. (1995) studied this dual capability of dispersants of increasing the surface area of dispersed oil and affecting the growth of hydrocarbon-degraders, and concluded that both of these factors influenced the effectiveness of dispersants at promoting oil decomposition. They found that increasing the sorbitan content of a dispersant stimulated oil biodegradation by acting as a nutrient source for the growth of hydrocarbon-degraders. In these studies little work has been done on the microbial interactions with oil droplets.

Herein are presented the results from two studies conducted between 1994 and 2001, into the effect ofa dispersant (Corexit 9500) on the dispersion, biodegradation and microbial colonisation ofboth Forties crude at 15 C and Alaskan North slope (ANS) oil at 8 C. Both studies were conducted using natural seawater in a Mackay apparatus designed to simulate the marine environment as closely as possible in laboratory conditions. In these studies droplet formation and size were analysed using a chamber slide technique adapted from Delvigne and Sweeney (1988).

Materials and Methods

The marine microcosms used throughout these two studies were based on the apparatus designed by

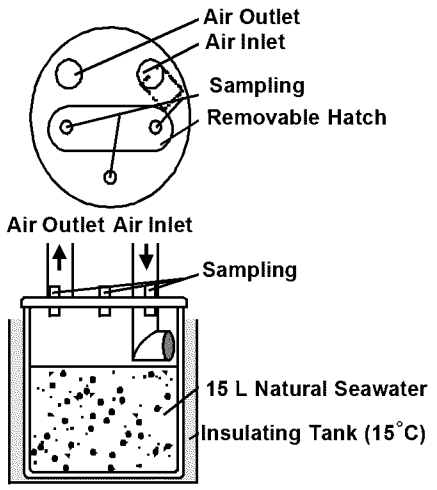

Fig. 1 Schematic ofthe laboratory microcosms.

Mackay and Szeto (1980), adapted and operated as described in Swannell et al. (1997) (Fig. 1). The Forties crude and ANS oils were weathered prior to use. Weathering was performed by distillation of the crude oil at 250 C, a process that removed approximately 25% of oil by weight (Walker et al., 1992). To simulate an oil slick, the weathered oil (10 ml) was added to each microcosm forming a slick approximately 100 Im thick, airflow was then switched on (5.0 ± 0.5 m/s), simulating the wind and wave action encountered at sea and was continued throughout each experiment.

Where required, chemical dispersion was achieved through the addition ofCorexit 9500 (10% w/w ofthe oil). Weathered oil (Forties or ANS) was added to the microcosm and held in a 50 mm diameter PTFE ring. Corexit 9500 was added evenly over the oil. The air flow was switched on and the ring removed, enabling the oil/dispersant mix to spread over the surface of the water.

For the study utilising Forties (study 1), 3 microcosms each containing 15 l seawater were set up as follows:

- Seawater containing oil and Corexit 9500;
- Seawater containing oil, Corexit 9500 and added levels ofnutrients (1 mg N-NO_3/l) simulating conditions found in estuarine and coastal waters in the UK;
- Seawater containing oil, Corexit 9500 and mercuric chloride (300 mg/l, Russell et al., 1992)—a killed control.

In addition, chemical dispersion was compared to natural dispersion (without dispersant) for nutrient amended, unamended and killed controls. Each study was carried out in triplicate at 15 C, conditions typ-

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ical ofthose in UK coastal waters. Throughout these microcosm experiments samples were taken on days 1, 2, 3, 5, 7, 9, 13, 16, 20, 23, and 27.

For the ANS oil (study 2), microcosms were set up as follows:

- Seawater containing ANS (the ffiatural dispersant test-);
- Seawater containing ANS and Corexit 9500;
- Seawater containing ANS, Corexit 9500 and mercuric chloride (300 mg/l)—the killed control.

On day 8 ofthe ANS study, microcosms were amended with 1 mg/l N as sodium nitrate and 0.1 mg/l P as potassium dihydrogen orthophosphate. Day 8 was chosen for nutrient addition as the team estimated that the original seawater nutrient content would become limiting by that time. This reduced the likelihood that the biodegradation ofoil by the indigenous microbial population would be limited by nitrogen or phosphorus over the course ofthe 35 days experiment.

Again, each microcosm study was carried out in triplicate, however the temperature was held at 8 C, conditions typical ofthose in Prince William Sound. Samples were taken on days 0, 1, 4, 7, 10, 14, 17, 21, 24, 28 and 35. For both Forties Crude and ANS experiments sampling consistency throughout was ensured by always using an open pipette from the same place and depth within the microcosm. Visual analysis confirmed that the microcosms remained single phased throughout each study. There was no visible formation of a water-in-oil emulsion.

To determine the impact ofdispersion on droplet formation, microbial biomass and oil degradation, the following analyses were performed common to both studies:

- Droplet formation (looking at both size and number ofdroplets using the Chamber slide method adapted from Delvigne and Sweeney (1988) by Swannell et al. (1997)), droplet size followed a Poisson distribution;
- Microbial biomass (most probable number counts) with the appropriate weathered oil as the C-source, Croft et al. (1995); and
- Oil degradation (GC/MS analysis total hydrocarbons (reported as n-alkane depletion in study 1); GC/MS analysis of the ratio of total hydrocarbons to the biomarker hopane in study 2 (Swannell et al., 1997)).

Analysis ofvariance was used to determine significant differences between microcosm treatments.

Results and Discussion

Study 1 (Forties)

Figure 2 presents semi-log plots ofthe droplet size and number following: (A) the addition of dispersant to the killed control, (B) the addition ofdispersant to natural seawater, and (C) the addition ofdispersant to nutrient amended natural seawater. In the killed control, by day 9 droplet number had reached the maximum detectable amount of4.5 $\cdot 10^6$ per ml and did not fall below this level for the remainder of the study. The majority ofdroplets in this microcosm were 1–2 Im in diameter. In contrast, in the presence of microorganisms the maximum droplet number was reached by day 9, but decreased from day 13 down to $<1 \cdot 10^6$ by the end ofthe study, significantly less than were detected in the killed control ($P < 0:05$). Finally, where nutrients were added, the pattern was similar to that for the dispersant amended seawater except that the peak concentration approximated to $3 \cdot 10^6$ by day 9 before falling off by day 16 (again a significant difference compared to the control ($P < 0:05$)). The decrease in final oil droplet numbers in the two ffive-

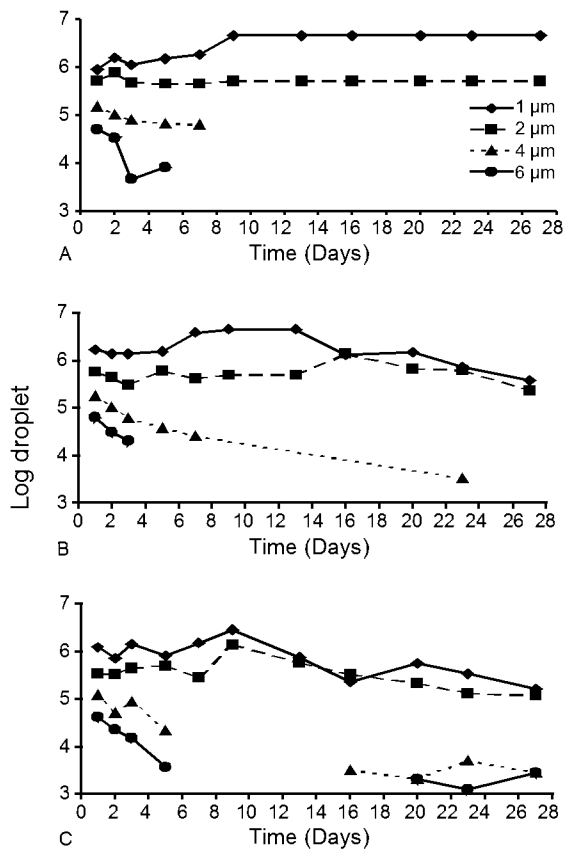

Fig. 2 Forties oil droplet distribution in seawater amended with (A) dispersant and mercuric chloride (the killed control); (B) dispersant; and (C) dispersant and low levels ofnutrient. The legend is presented in A.

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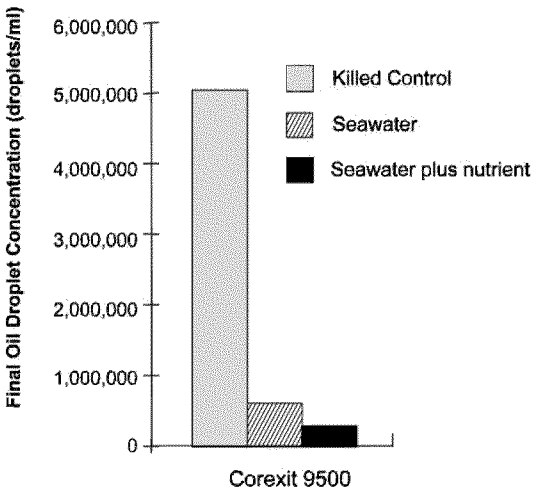

Fig. 3 Reduction in Forties oil droplet concentration in the killed control, seawater and seawater with low levels ofnutrients.

microcosms compared to the killed control is shown in Fig. 3. These results suggest microbial degradation of the dispersed oil droplets in the dispersant amended seawater samples, with said degradation further stimulated by the presence ofa low concentration of additional nutrients.

Analysis ofthe n-alkane depletion in comparison to that in the killed control confirmed this finding, with approximately 90 and 55% of the n-alkanes degraded in the nutrient amended seawater and the non nutrient amended seawater, respectively (Fig. 4(A)). The impact of the dispersant on the microbial population is illustrated in Fig. 4(B) showing the difference in mean maximum microbial growth as measured by MPN/ml/day in the chemically dispersed verses the naturally dispersed Forties crude with and without added nutrients. Max MPN/ml/day were an order of magnitude

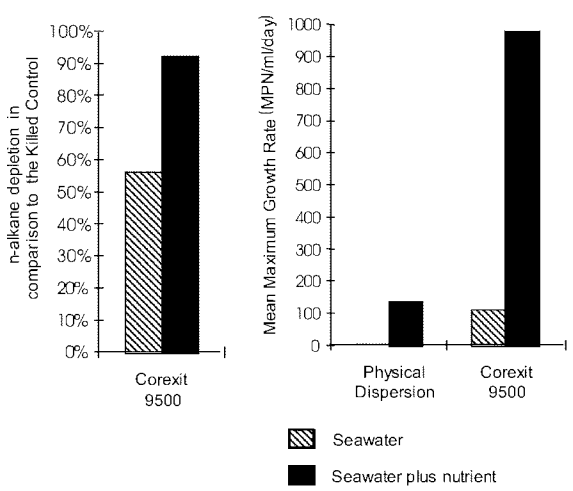

Fig. 4 (A) Depletion ofForties n-alkanes compared to the killed control for seawater with dispersant and seawater, dispersant and low levels of nutrient, and (B) impact of dispersant on microbial growth rate in seawater and seawater with low levels of nutrient.

greater in the chemically dispersed microcosms verses those without dispersant.

Study 2 (ANS)

Results obtained during the ANS slope study at 8 C were more variable than those for the Forties crude at 15 C. Oil droplet size and distribution are presented in Fig. 5(A) and (B) and in Table 1 (the large variation making it impossible to show this result as a figure). This contrasted with the lower variation in the Forties experiment. In the killed controls, oil dispersion was characterised by high numbers ofoil droplets at the start ofthe experiment that depleted with time (30–53% decrease in droplet number, Fig. 5(A)). The oil droplet size distribution showed that large oil droplets present at the start ofthe experiment disappeared over time, consistent with the hypothesis that large oil droplets re-coalesced with the oil slick. Where dispersant was added, the droplet counts pattern was again characterised by high numbers ofoil droplets at the start ofthe experiment that decreased with time (Fig. 5(B)). However the decrease in oil droplet numbers was significantly greater in these microbiologically active microcosms than in the killed controls, with 86–95% depletion in the total number ofoil droplets by the end ofthe experiment ($P < 0:05$). This observation may reflect the biodegradation ofthe oil droplets by indigenous hydrocarbon-degraders over

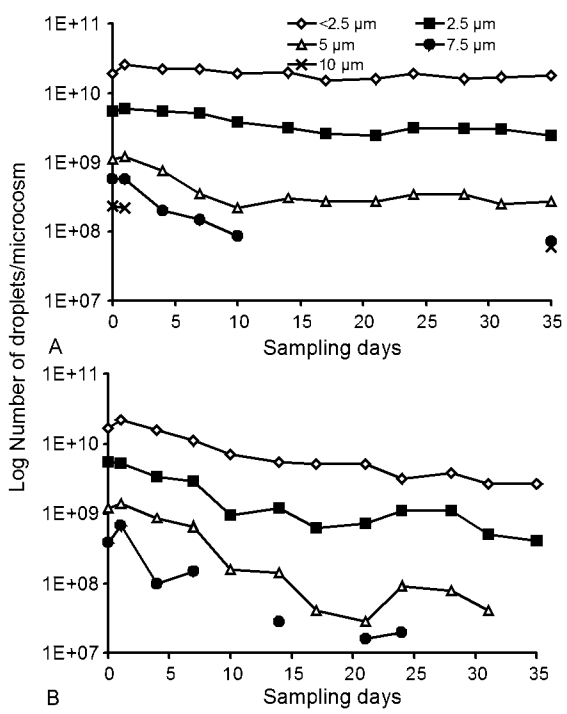

Fig. 5 ANS oil droplet distribution in seawater amended with (A) dispersant and mercuric chloride (the killed control); and (B) dispersant. The legend is presented in A.

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Table 1 Oil droplet distribution in replicate natural dispersion microcosms (ANS study) over time (days)

	7	10	14	17	21	24	28	31	35
Exp 1									
<2.5	7.80	1.25	31	79.3	149	246	125	85.4	41.2
2.5	3.40	0.31		5.45	15.6	39.8	26.3	4.68	3.07
5	1.28					5.16	7.66		
7.5	0.14					1.47			
10									
Exp 2									
<2.5		1.87	5.10	1.20	110	151	278	564	850
2.5		0.47	2.32	0.96	22.7	38.5	43.8	130	74.2
5					3.98	1.75	1.75	12.0	2.39
7.5							0.88	8.58	
10									
Exp 3									
<2.5	1.76	2.76	32.6	57.5	23.9	9.50	4.01	3.88	6.67
2.5			14.0	23.3	12.5	4.75			0.95
5			0.93	3.11	1.04	0.95			
7.5				1.55					
10									

Numbers represent droplets per microcosm ($\cdot 10^7$).

time. The oil droplet size distribution was similar to that observed with the controls, with larger droplet numbers decreasing over time. To a lesser extent than was noted for the killed controls, the number of oil droplets produced still varied substantially between replicates, again reflected in the large standard deviations.

For the natural dispersion tests, the oil slick emulsified to different extents in each replicate, showing a greater degree ofvariability than observed previously with the Forties crude oil at 15 C. This resulted in three different patterns ofoil dispersion (Table 1). In replicate 1, the pattern ofoil dispersion was characterised by the appearance ofa low number ofoil droplets by day 7, increasing to a maximum on day 24 and then decreasing up to the end ofthe experiment. In contrast the oil in replicate 2 emulsified to the extent of forming a "mat" of oil on the surface of the water. Possibly as a result ofthis, the onset ofoil dispersion was delayed until day 10. By day 21 the oil droplet numbers started to increase and, in contrast to that observed in replicate 1, continued to increase until day 35. In the final replicate, the oil slick again emulsified before forming a semi-submerged "ball" of oil and water reducing the surface area of the oil slick. Consequently, this microcosm contained the lowest total number ofoil droplets. In general, a higher number ofoil droplets were noted in the ANS natural dispersion microcosms than in the Forties crude microcosms (Swannell & Daniel, 1999).

Although a consistent pattern ofdroplet distribution was observed for the ANS oil (at least in the killed control and chemical dispersant tests, less so in the natural dispersant test), the number ofoil droplets produced varied substantially between replicates. This finding was at odds with the results from the Forties crude study. This variation in results could be a reflection ofboth the different oil types (ANS is less dispersible and the oil may form a less stable oil-in-water emulsion than Forties in the presence of Corexit 9500), and the temperature (8 C in the ANS verses 15 C for the Forties). The lower temperature may have reduced the stability ofthe dispersed phase and the effectiveness ofthe dispersant.

During the microscopic enumeration ofthe ANS oil droplets, bacterial colonisation ofthe oil droplets was assessed. In microcosms treated with dispersant, by day 4 at least 40 % ofthe oil droplets were colonised by 1 or more bacteria (Fig. 6). The percentage of colonised bacteria increased to approximately 80% by day 17 and stayed at that level for the remainder of the experiments. Thus, in the presence ofdispersant the oil droplets became colonised within days, and bacteria-oil-protozoa and nematode droplet clusters formed of 10 Im to 1–2 mm, a finding also observed in the

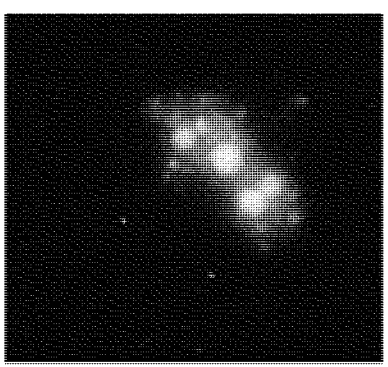

Fig. 6 Cluster ofoil droplet and bacteria under epifluorescence at a magnification of400 ·, the biggest oil droplet diameter is 5 Im.

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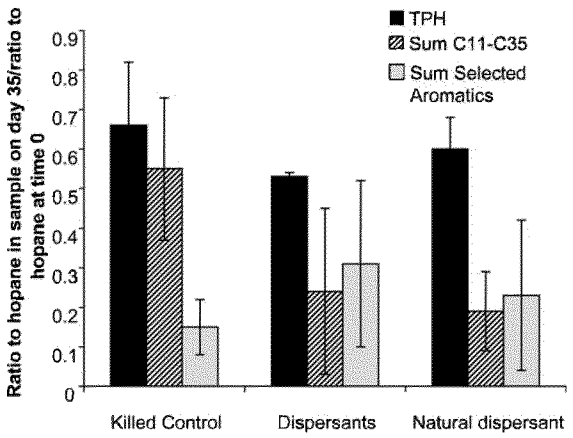

Fig. 7 Ratio ofTPH, the sum ofthe C11 to C35 n-alkanes and the sum of selected aromatics to the biomarker hopane on day 35 of the ANS study to hopane at time 0 (error bars represent standard deviation). Selected aromatics are: (naphthalene, methylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes, dibenzothiophene, methyldibenzothiophenes, dimethyldibenzothiophenes, phenanthrene, methylphenanthrenes, and dimethylphenanthrenes).

Forties crude oil study. Similar findings were observed in the natural dispersion microcosms with clusters observed shortly after the onset of oil dispersion (day 10–14). As in the Forties study, the oil droplet colonisation results show that the indigenous microbial populations are interacting closely with the oil and presumably biodegrading it.

To assess the extent ofbiodegradation at the end of the study (day 35) concentrations ofselected biodegradable fractions of oil were compared with the recalcitrant biomarker hopane. Results are presented as the ratio ofthe total volumes ofpetroleum hydrocarbons (TPH), the sum ofthe C11 to C35 n-alkanes, and the sum of selected aromatics, to hopane (Fig. 7). Although the ratio of TPH and n-alkanes to hopane on day 35 was lower in the chemically and naturally dispersed microcosms than in the killed controls, variation between replicates meant this decrease was not significant (P > 0:05). Similarly, there was no significant difference in the ratio of the selected aromatics to hopane between the killed controls and the

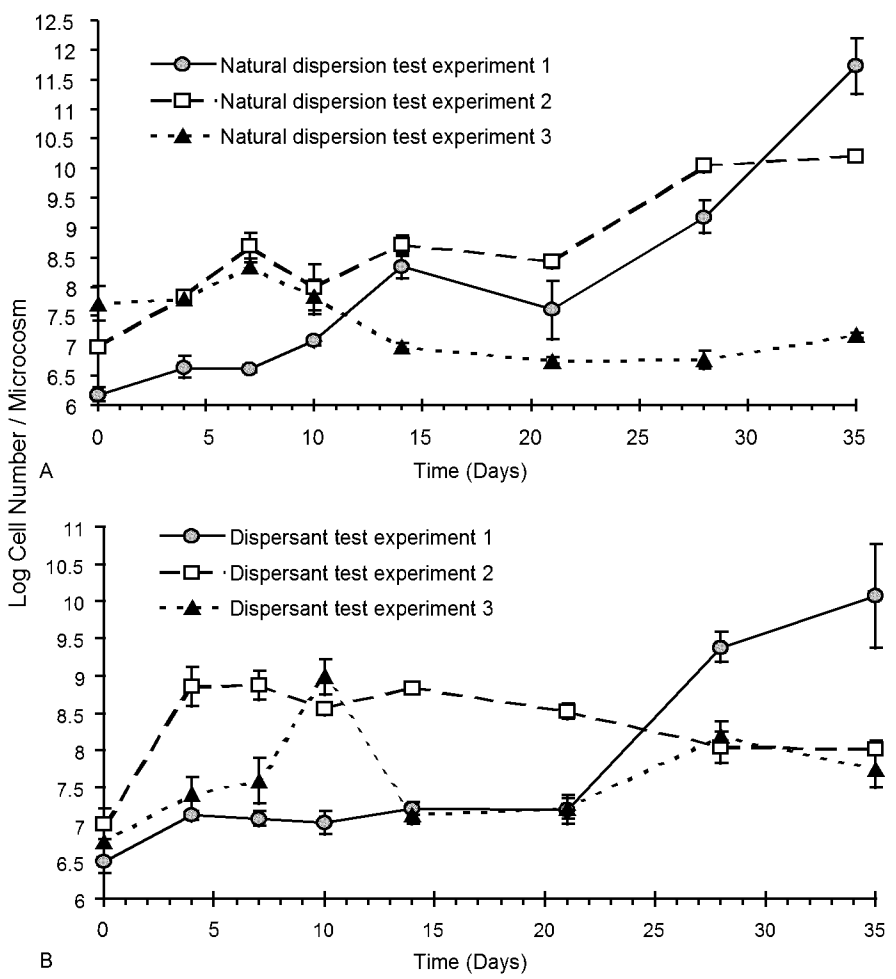

Fig. 8 Hydrocarbon degrading populations in the biologically active ANS study microcosms: (A), natural dispersion experiment; (B), chemical dispersant test (error bars represent the standard deviation).

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dispersion tests (P > 0:05). By comparison, a significant decrease in the ratio of n-alkanes to hopane in chemically dispersed oil compared to killed controls was detected in the Forties crude study (Swannell & Daniel, 1999), indicating biodegradation at 15 C. The loss of hydrocarbons in the killed control was probably the result of evaporation. In the Forties Experiment, the addition of Corexit 9500 resulted in all the oil becoming dispersed and remaining in the water column, thereby reducing additional evaporation. With the ANS, a significant percentage of the oil remained undispersed, potentially increasing the evaporation.

The killed controls from the ANS study did not contain any bacteria as quantified by MPN counts. In both natural and chemical dispersant tests, the MPN counts exhibited a large variation between replicates. For both treatments there was an initial increase in the hydrocarbon-degrading population in all replicates (Fig. 8(A) & (B)). After this initial increase, the hydrocarbon-degrading population ofthe chemical dispersed replicates stabilised over time (Fig. 8(B)) with only replicate 1 exhibiting a significant subsequent increase in MPN counts (an increase ofapproximately 3 orders ofmagnitude by day 35). In replicates 1 and 2 ofthe naturally dispersed microcosms (Fig. 8(A)), however, MPN counts increased over time (by between 3 and 5 orders ofmagnitude by day 35), a pattern that was not repeated in replicate 3. Variation between experiments could be explained by the formation ofclusters. This finding correlated with the lower number ofoil droplets detected in this replicate. Maximum growth rates in the presence ofthe chemical dispersant were approximately one fifth of those observed with Forties crude at 15 C, presumably reflecting slower growth on oil at the lower temperature, an observation made by other researchers (Leahy & Colwell, 1990). However, in the naturally dispersed treatments, microbial growth rates were higher in the ANS samples than had been detected in the Forties study. This result reflected the greater droplet number seen with natural dispersion ofthe ANS at 8 C compared to the Forties at 15 C.

Conclusions

For both Forties crude and ANS oil, the addition of dispersant resulted in increased oil droplet numbers in comparison to natural dispersion. However, the results ofthe killed controls suggested that the oil-in-water emulsion was not as stable with ANS and Corexit 9500 at 8 C as it was with Forties and Corexit 9500 at 15 C. For both oil types, natural processes promoted oil dispersion with microbial colonisation, albeit at lower levels for the Forties crude at 15 C than those observed for the ANS at 8 C. Oil degraders proliferated in all biologically-active microcosms with bacteria colonising the oil droplets forming large bacteria-oil-protozoa-nematode clusters. However, compared to the killed controls, oil biodegradation was confirmed only in the Forties crude study at 15 C.

The results ofthis study suggest that the fundamental microbiological processes that occur after chemical dispersion ofoil in the sea are similar for both Forties and ANS. In both cases, dispersed droplets were colonised within days by bacteria, coalescing to form clusters of droplets and bacteria. This process coincides with an increase in the local numbers ofindigenous hydrocarbon degraders. However, temperature, and possibly oil type, has a large effect on dispersion and microbial growth rate and biodegradation ofoil. It should be remembered that these experiments were conducted in contained microcosms, whereas in open water dispersion also dilutes and disperses the oil and where nutrients may not become limiting.

Given the differences between the experiments, the influence oftemperature on the dispersion ofForties and ANS deserves further investigation, particularly as at higher temperatures the residence time ofdispersed oil in the water column could be significantly shorter. Moreover, these laboratory observations require field evaluation to confirm that they are representative ofthe natural marine ecosystem. Field studies however present a significant challenge to researchers.

Acknowledgements—This work was funded through grants from The Department ofEnvironment, Transport and the Regions (DETR-UK); Minerals Management Service (MMS), Alaska Department ofEnvironmental Conservation (ADEC) and US Coast Guard (USCG).

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The primary biodegradation of dispersed crude oil in the sea

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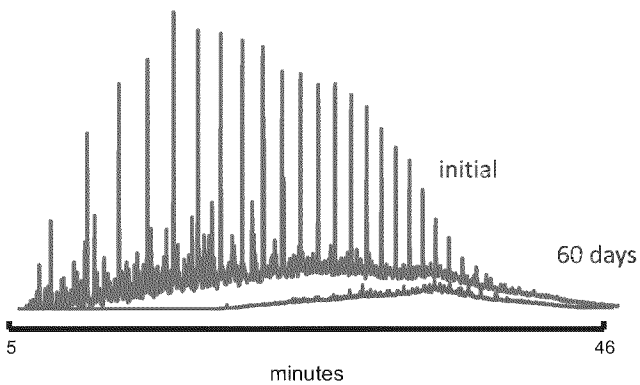
HIGHLIGHTS

- Dispersed crude oil is rapidly and extensively biodegraded in natural seawater.
- This occurs without the need for added nutrients or bacteria.
- This biodegradation extends to all resolvable classes of hydrocarbons except the hopanes.
- The approximate biodegradation half-life is 11–14 d.

GRAPHICAL ABSTRACT



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ABSTRACT

Dispersants are important tools for stimulating the biodegradation of large oil spills. They are essentially a bioremediation tool – aiming to stimulate the natural process of aerobic oil biodegradation by dispersing oil into micron-sized droplets that become so dilute in the water column that the natural levels of biologically available nitrogen, phosphorus and oxygen are sufficient for microbial growth. Many studies demonstrate the efficacy of dispersants in getting oil off the water surface. Here we show that biodegradation of dispersed oil is prompt and extensive when oil is present at the ppm levels expected from a successful application of dispersants – more than 80% of the hydrocarbons of lightly weathered Alaska North Slope crude oil were degraded in 60 d at 8 °C in unamended New Jersey (USA) seawater when the oil was present at 2.5 ppm by volume. The apparent halftime of the biodegradation of the hydrocarbons was 13.8 d in the absence of dispersant, and 11 d in the presence of Corexit 9500 – similar to rates extrapolated from the field in the Deepwater Horizon response.

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1. Introduction

Large amounts of crude oil have been entering the world's oceans for millions of years, and a diverse group of microorganisms has evolved to take advantage of this rich source of reduced carbon (Prince, 2010; Prince et al., 2010). Much of the oil comes from natural seeps, and while some adheres to sediment particles and is degraded on the sea bottom, some rises to the sea surface to form slicks, and some disperses as small droplets in the water column (Farwell et al., 2009). Other oil comes from anthropogenic sources, both as runoff from land and from drilling and shipping accidents (National Research Council, 2003). Oil is an unusual substrate in two main regards. First, only a few molecules such as the smallest saturates (e.g. methane, ethane and propane) and aromatics (e.g. benzene, toluene, ethylbenzene and the xylenes) are significantly soluble – so biodegradation of most oil components must take place at the surface of the oil. Second, while oil provides a rich

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source of carbon and energy, it contains no significant amounts of biologically available nitrogen or phosphorus essential for microbial growth. Together these mean that the biodegradation of significant amounts of oil in aerobic environments is likely to be limited by the available surface area of the oil, and the presence of nutrients. The biodegradation of oil on shorelines has been enhanced by the judicious application of fertilizers to the oil (Bragg et al., 1994; Prince and Bragg, 1997), but adding nutrients to slicks on the open ocean is not usually appropriate in view of the likely competition for uptake by planktonic photoautotrophs. Instead the preferred approach for stimulating the biodegradation of oil slicks and subsea releases is to add chemical dispersants to substantially increase the surface to volume ratio of the oil, and allow the oil to disperse so that the natural background levels of biologically available nitrogen or phosphorus are adequate for microbial growth (National Research Council, 2005). For example, dispersants were used on a large scale following the spill from the *Sea Empress* in South Wales (Lunel et al., 1997), and more recently at the leaking wellhead of the *Deepwater Horizon* blowout in the Gulf of Mexico (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011).

Despite these large-scale uses, and many tests of the effectiveness of dispersants in dispersing crude oil, from laboratory through large tanks, field trials and actual use (e.g. Mukherjee and Wrenn, 2009; Li et al., 2009a,b; Belore et al., 2009; Lewis et al., 2010), few papers have addressed the question of the biodegradation of dispersed oil under environmentally relevant conditions. Oil slicks of light to medium oils spread rapidly until they are only approximately 100 μm or less in thickness (Lehr et al., 2002). Applying dispersant to such a slick in 1-m waves causes nearly immediate mixing of dispersed oil into the top 1–1.5 m of the water column (Delvigne and Sweeney, 1988), resulting in immediate dilution by a factor of about 10000 to give an average oil concentration of ~100 ppm (Belore et al., 2009). The dispersed droplets are so small, typically 10–100 μm in diameter (Li et al., 2011), that they are entrained in the water column as discrete droplets that do not coalesce but diffuse to ever more dilute concentrations. It is technically challenging to do biodegradation experiments at such dilutions, and no published work that we have found (Bruheim et al., 1999; Lindstrom and Braddock, 2002; MacNaughton et al., 2003; Venosa and Holder, 2007; Zahed et al., 2010) comes very close.

We report here the biodegradation of fresh and lightly weathered crude oil (the latter mimicking exposure at sea for 24 h) with and without the dispersant Corexit 9500 (Nalco, 2011), at concentrations approaching those seen following a real spill in natural seawater with no added nutrients or bacteria. This mimics the conditions for natural biodegradation, but at the expense of demonstrating the physical effectiveness of the dispersant – at such concentrations, and in stirred laboratory experiments, Alaska North Slope crude oil disperses quite well with no additions. We show that oil is extensively degraded under such conditions, and that Corexit 9500 exerts no inhibitory effects.

2. Materials and methods

Seawater was collected from the New Jersey shore in April 2010 and January and April 2011 (winter conditions, salinity = ~28 ppt, temperature = ~8 °C). Nitrate and phosphate levels were below detection limits with simple laboratory colorimetric tests, but are likely to have been near 7 and 0.5 μM respectively (Louanchi and Najjar, 2001). The seawater was transferred to a cold room at 8 °C and aerated for 24 h prior to assembly of the experiments in 5 L carboys. Four liters of seawater were placed in each carboy, and were stirred with a large magnetic stirrer to generate a 2 cm vortex. We tried two methods of adding oil to these vessels, with indistinguishable biodegradation results. In the first, Alaska North Slope crude oil was weathered by evaporation at laboratory room temperature in a hood until it had lost 20% of its weight. Corexit 9500 was added at 5% to an aliquot, and 10 μL of the weathered oil or weathered oil plus dispersant was added to each carboy (both in triplicate) with a positive displacement pipette to yield 2.5 ppm oil by volume. As shown below, these experiments revealed no substantial difference in the extensive biodegradation seen after 60 d. In the second pair of experiments, 10 μL of fresh Alaska North Slope crude oil was added to the 4 L batches of seawater without dispersant: the dispersed oil was generated by floating 1 mL of oil on 1 L of seawater in an aspirator vessel. The water was stirred vigorously with a magnetic stir bar to generate a 2 cm vortex, and 67 μL of Corexit 9500 was dropped on the slick with a positive displacement pipette. The oil instantly dispersed throughout the water column, and after 2 min of stirring the stirrer was turned off and the contents allowed to settle for a few minutes. Dispersed oil was drawn off from the bottom of the aspirator bottle, and 10 mL of the dispersed oil/water mixture was added to 4 L of seawater. In this case enough replicate vessels were assembled, in two separate campaigns, that duplicate carboys of oil with and without Corexit could be sacrificed at 0, 4, 6, 11, 24 and 41 d.

At the designated time, oil was extracted from each carboy, three times, with methylene chloride, dried with sodium sulfate, and analyzed by gas chromatography coupled with mass spectrometry (Douglas et al., 1992). Care was taken to prevent complete evaporation of the methylene chloride so as not to lose volatile oil components during extraction. Oil biodegradation was followed with respect to 17α(H),21β(H)-hopane as a conserved internal marker within the oil (Prince et al., 1994). Apparent half-times of the loss of analytes were calculated as before (Prince et al., 2007). Two-dimensional GC followed earlier methods (Wang et al., 2003), but used a flame ionization detector; the first column separated the oil components by boiling point, the second by polarity. This approach separates the oil into eight major classes: 3-ring aromatics, 2-ring aromatic + 1-saturated ring or 5-saturated rings, 2-ring aromatics or 4-saturated rings, 1-ring aromatic + 1-saturated ring or 3-saturated rings, 1-ring aromatic or 2-saturated rings, 1-saturated ring, alkanes, and hopanes.

3. Results

Fig. 1 shows total ion chromatograms of the initial oils and oils extracted after biodegradation with the natural indigenous microbiota and nutrients at 8 °C. The top trace is the original oil before addition to the seawater; the sample with Corexit had this added to the neat oil, although the experiment used oil dispersed by addition of the dispersant to the oil on the water surface, as described above. It is noteworthy that the initial sample with dispersant shows prominent peaks near 28 min that are not seen in the samples extracted from the water phase – these are some of the surfactant molecules (Nalco, 2011) that are not extractable from water with methylene chloride. On the other hand, the features near 14 min can be attributed to the hydrocarbon solvent of the dispersant (Nalco, 2011) – these are extracted from water with our protocol, as shown in the samples labeled Day 0. These samples were extracted within 10 min of the initial assembly of the experimental systems, and it is noteworthy that in this time the samples without dispersant had lost most hydrocarbons smaller than naphthalene. The evaporative loss was much reduced in the dispersed sample, presumably because the hydrocarbons were in the bulk water phase.

The oils were extensively and rapidly degraded, with both the alkanes responsible for the sharp peaks and the unresolved material showing substantial losses. Very similar extensive biodegrada-

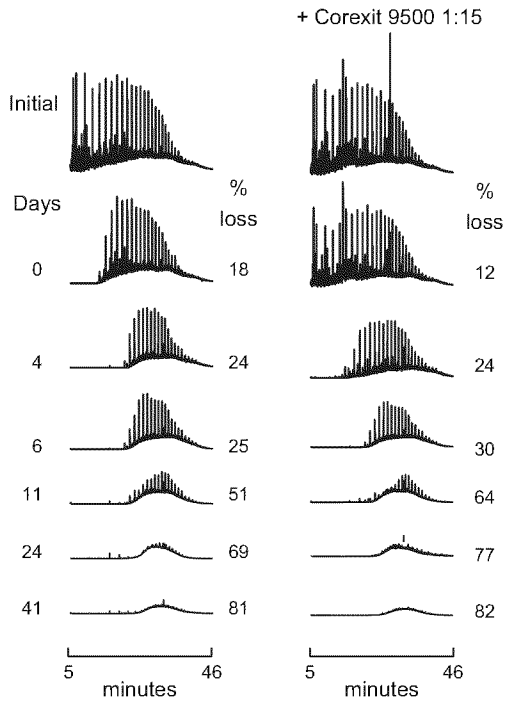

Fig. 1. Total ion chromatograms of fresh crude oil without and with 6.7% Corexit 9500 at the beginning of the incubation, and after the indicated days of stirring in unamended seawater at 8 °C. The 'initial sample' with Corexit is actually a sample of fresh oil plus Corexit, while the experimental samples had the dispersant added to oil floating on water as described in Section 2.

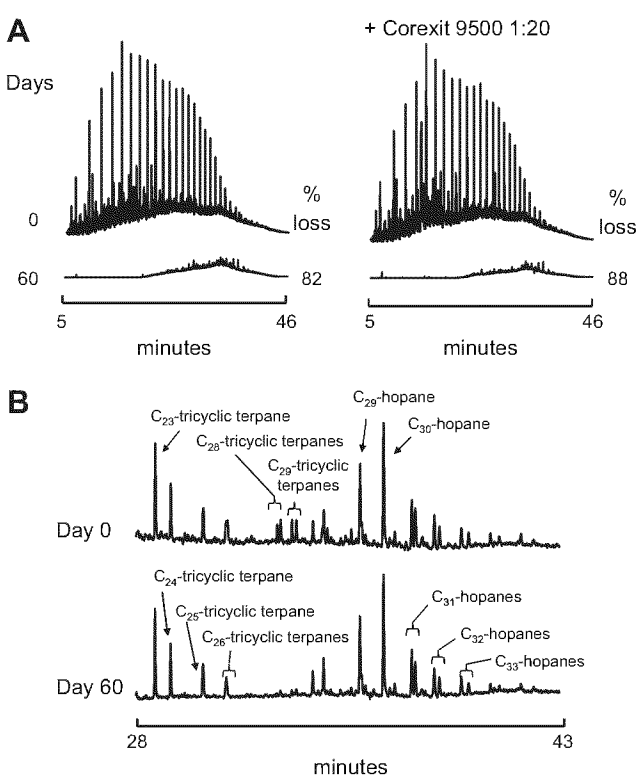

Fig. 2. (A) Total ion chromatograms of artificially weathered crude oil without and with 5% Corexit 9500 at the beginning of the incubation, and after 60 d of stirring in unamended seawater at 8 °C. The Corexit was added to the oil prior to addition to the flask. (B) $m/z = 191$ chromatograms of the initial oil and biodegraded samples with Corexit.

tion was seen when the experiment used 20% weathered crude oil as shown in Fig. 2A. These losses can be quantified using 17α(H),21β(H)-hopane as a conserved internal marker within the oil (Prince et al., 1994). Although hopanes are eventually biodegraded (Prince and Walters, 2007), this process does not appear to have happened in our experiments (Fig. 2B), although there was biodegradation of the C_{28} and C_{29} tricyclic terpanes after 60 d. If 17α(H),21β(H)-hopane had been degraded in our experiments, our estimates of the extent of biodegradation would be underestimates. The biodegradation of representative alkanes and aromatics in the oil are shown in Fig. 3. The essentially complete loss of all the alkylnaphthalenes likely includes some evaporative losses, but the losses of the other aromatics can be principally attributed to biodegradation (Prince and Walters, 2007). Unfortunately GC/MS cannot readily quantify all the individual hydrocarbons of crude oil. The major groups of compounds can, however, be separated using two-dimensional gas chromatography with flame ionization detection, as shown in Fig. 4. Fig. 5 compares the initial oil with samples of weathered oil after 60 d of biodegradation. It is clear that all the resolved components have undergone substantial loss, with the exception of the hopanes. This includes the aromatic compounds with up to at least three rings, the saturated ring compounds with up to at least five rings, multi-ring compounds with both aromatic and saturated rings, and the linear and branched alkanes.

We have enough replicates ($n = 10$) that we can calculate the median apparent half-lives of primary biodegradation of some individual analytes, and these are listed in Table 1. The apparent

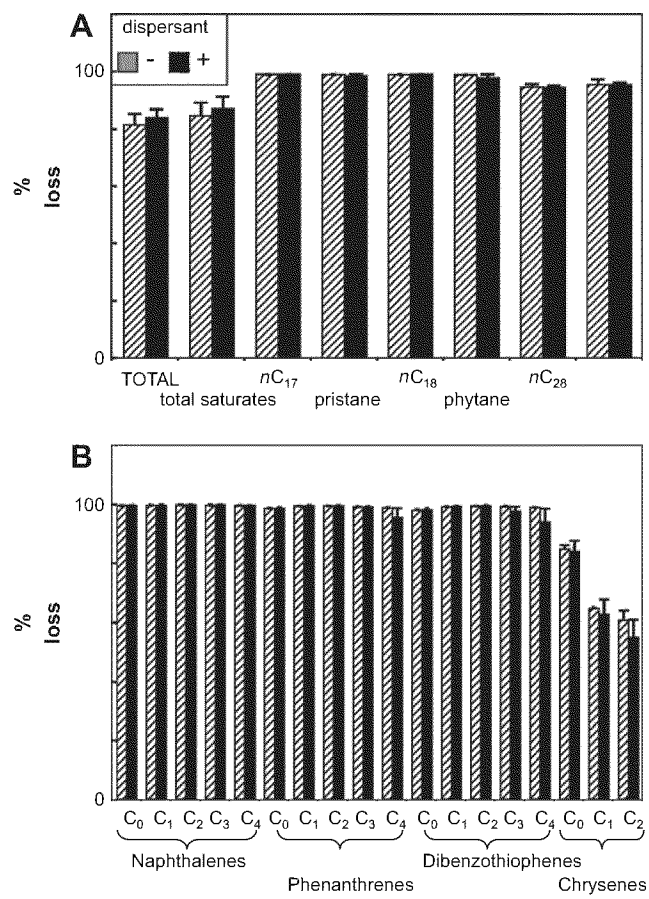

Fig. 3. Loss of (A) total resolved hydrocarbons, total saturates (measured as $m/z = 57$) and representative alkanes, and (B) representative polycyclic aromatic hydrocarbons in the samples of Fig. 2. The C_n nomenclature indicates the number of alkyl carbons on the aromatic nucleus; C_3 for example, includes trimethyl, methylethyl, propyl and isopropyl forms. The error bars are standard errors.

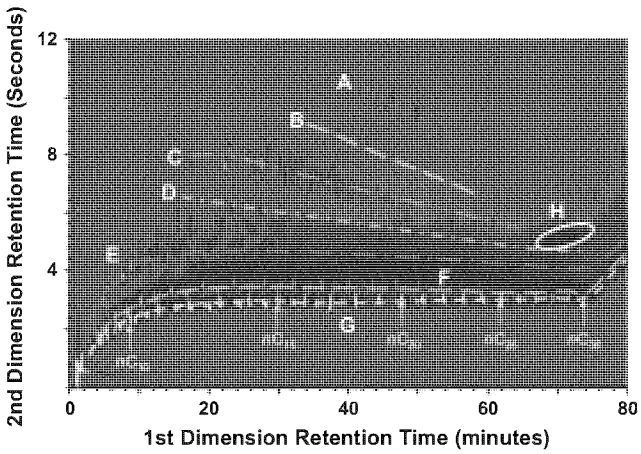

Fig. 4. Two-dimensional GC chromatogram of the initial, partially weathered oil. The first dimension separates by boiling point, the second by polarity. A: 3-ring aromatics series. B: 2- ring aromatic + 1-saturated ring or 5-saturated ring series. C: 2-ring aromatics or 4-saturated ring series. D: 1-ring aromatic + 1-saturated ring or 3-saturated ring series. E: 1-ring aromatic or 2-saturated ring series. F: 1-saturated ring series. G. alkane series – representative n-alkanes are identified. H: hopane series.

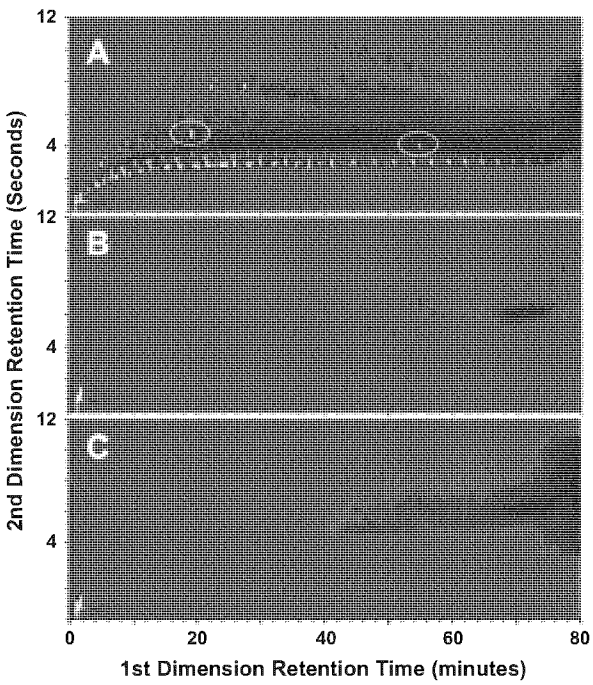

Fig. 5. Two-dimensional GC chromatogram of the initial, partially weathered oil with dispersant (A), and the biodegraded oils with (B) and without (C) dispersant. Components attributable to the dispersant (Nalco, 2011), not present in Fig. 5, are enclosed in ellipses.

half-lives are calculated from the amounts remaining at various times, and they do not include the clear lag-times apparent in Fig. 1. Nevertheless they provide an indication of how rapidly oil can disappear from the environment when it is dispersed at low concentrations. As expected (Douglas et al., 1996), phenanthrenes and dibenzothiophenes were degraded at essentially similar rates, while chrysenes were more resistant to biodegradation, with or without dispersant. It is noteworthy that all the isomers of the alkyl aromatics of Fig. 3 are degraded – 3-methylchrysene is apparently the least degradable methylchrysene, but its degradation was clearly underway at the end of the experiment (Fig. 6). There have been reports that dispersants inhibit the biodegradation of polycyclic aromatic hydrocarbons (Lindstrom and Braddock, 2002) and sulfur containing species such as the dibenzothiophenes (Foght et al., 1983). Neither effect is seen in our experiments.

4. Discussion

Many earlier experiments (e.g. Bruheim et al., 1999; Lindstrom and Braddock, 2002; MacNaughton et al., 2003; Venosa and Holder, 2007; Zahed et al., 2010) used rather higher concentrations of oil and additional nutrients to allow its degradation. A classical medium, used by many, is that of Bushnell and Haas (1941), which provides 25 mM bioavailable nitrogen as a combination of nitrate and ammonium, and 13 mM phosphate. The medium was developed during World War II for studying biodegradation in fuel storage facilities, and it is really quite inappropriate for mimicking marine systems where the levels of nutrients are many orders of magnitude lower. Such high levels might well alter the relative competitive advantage of the microbial populations. Even nearshore Atlantic waters contain only a few micromolar available nitrogen (Levitus et al., 1993; Louanchi and Najjar, 2001; Pelegri et al., 2006; While and Haines, 2010), and less than micromolar phosphate, and most of the world's oceans have only nanomolar concentrations of nutrients (Patey et al., 2010). Clearly these natural levels of nutrients, and the native biota of fresh seawater are adequate for substantial biodegradation of dilute hydrocarbons.

We note that our measurements detect only the hydrocarbons in crude oil, and do not address the potential biodegradability of the asphaltenes and resins (Tissot and Welte, 1984). Furthermore, the disappearance of analytes minimally indicates only the initiation of the biodegradation process – commonly known as primary biodegradation – not their ultimate biological oxidation to water and CO_2. Quite likely much of the carbon is still in the microbial biomass in our experiments – Yerushalmi and Guiot (1998) concluded that the biomass yield of microbes growing on gasoline varied from 0.43 mg/mg to 0.69 mg/mg, and it seems reasonable that these values might be representative of many degradable hydrocarbons. Beolchini et al. (2010) estimated a value of 0.39 mg biomass/mg of hydrocarbons in harbor sediments, which likely contain significant amounts of recalcitrant hydrocarbons since the most readily biodegraded would likely already have been consumed. It has long been recognized that hydrocarbon-degrading organisms incorporate hydrocarbons into cellular lipids (Davis, 1964; Mazzella et al., 2005) and storage products (Klein et al., 2008; Manilla-Pérez et al., 2010; Rontani, 2010). These enter the ocean foodweb, and may eventually give rise to enhanced fisheries (Levy and Lee, 1988).

5. Conclusions

Our experiments demonstrate that even under late winter conditions, in our case a water temperature of 8 °C, the primary biodegradation of oil in seawater can be reasonably rapid, with no additional nutrients, when the concentration of oil is in the few ppm. These are the concentrations likely to occur after a successful application of dispersant (National Research Council, 2005). Recent data from the Gulf of Mexico suggesting the similarly rapid biodegradation of oil dispersed at the sea bottom from the Deepwater Horizon blowout (Hazen et al., 2010), with a lag of several days before biodegradation got underway (Reddy et al., in press), are fully concordant with our findings.

It is important to recognize that the simple comparison of the rate of biodegradation in the presence and absence of dispersant in Table 1 is somewhat misleading in judging the effectiveness of dispersants. As we have shown, the biodegradation of dispersed

Table 1
Initial concentrations and median apparent half-lives of primary biodegradation of some individual analytes. The concentrations assume full solubility in the total volume.

	Initial concentration (ppb)	Median apparent half-life (d)	Median apparent half-life with dispersant (d)
Total detectable hydrocarbons		13.8	11.0
Total saturates ($m/z = 57$)		15.6	11.6
17α(H),21β(H)-hopane	0.48		
Heptadecane	9.24	1.9	1.8
Pristane	4.87	4.7	3.4
Octadecane	5.48	2.5	2.2
Phytane	3.36	5.3	3.8
Triacontane	1.85	13.1	7.8
Naphthalene	1.35	2.3	1.9
C_1-naphthalenes	2.96	2.0	1.7
C_2-naphthalenes	3.73	1.9	1.7
C_3-naphthalenes	2.88	1.9	1.8
C_4-naphthalenes	1.46	2.1	1.9
Fluorene	0.20	3.1	2.6
Phenanthrene	0.56	2.6	2.2
1-Methylphenanthrene	0.36	2.8	2.4
2-Methylphenanthrene	0.27	2.9	2.5
3-Methylphenanthrene	0.22	3.0	2.6
9-Methylphenanthrene	0.41	3.5	2.5
C_2-phenanthrenes	1.48	7.9	9.7
C_3-phenanthrenes	1.05	18.9	22.4
C_4-phenanthrenes	0.63	28.8	35.7
Dibenzothiophene	0.49	2.7	2.4
1-Methyldibenzothiophene	0.17	3.7	4.5
2/3-Methyldibenzothiophenes	0.27	3.0	3.5
4-Methyldibenzothiophene	0.51	2.8	3.5
C_2-dibenzothiophenes	1.43	7.8	7.6
C_3-dihenzothiophenes	1.26	19.5	21.2
C_4-dibenzothiophenes	0.69	33.3	35.9
Benz[a]anthracene	0.03	26.6	17.8
Chrysene	0.10	30.8	36.2
1-Methylchrysene	0.02	14.3	14.3
2-Methylchrysene	0.02	6.3	11.2
3-Methylchrysene	0.11	27.1	36.5
4/6-Methylchrysenes	0.02	11.3	12.4
C_2-chrysenes	0.25	28.1	28.5
Sum 16 EPA priority pollutants	2.24	4.5	4.0

The C_n nomenclature indicates the number of alkyl carbons on the aromatic nucleus; C_3 for example, includes trimethyl, methyl-ethyl, propyl and isopropyl forms. 2- and 3-methyldibenzothiphenes co-elute, as do 4- and 6-methylchrysenes. 5-methylchrysene is below detection. Most of the EPA priority pollutants (Keith and Telliard, 1979) are below detection limits in our experiments; the predominant components are naphthalene and phenanthrene.

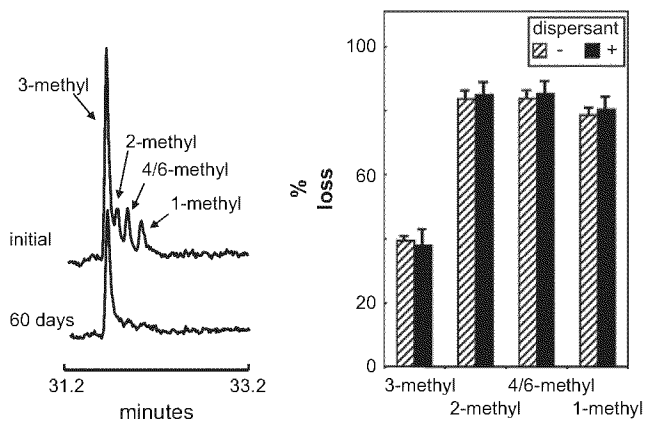

Fig. 6. Loss of methyl chrysenes. The chromatograms are of $m/z = 242$. 4-and 6-methylchrysenes co-elute under our conditions.

oil at the few ppm level is not significantly stimulated by dispersant addition. But this misses the point that dispersants are only used for significant spills – to remove slicks from the water surface, and prevent the formation of water-in-oil mousses and the stranding of oil on shorelines. The rate of biodegradation of heavy concentrations of undispersed oil is much slower than seen here, limited by surface area and nutrient availability, and likely also by oxygen access. The role of dispersants is not to stimulate the biodegradation of dispersed oil, but to allow the dispersion. We show here that the biodegradation of dispersed oil is essentially unaffected and certainly not inhibited by the presence of dispersants, and is rapid and extensive.

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Biodegradation of Non-Ionic Dispersants in Sea-Water

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Summary. In this paper, we describe the aerobic biodegradation of some non-ionic dispersants of the Span, Tween, and Corexit series in sea-water, where they are now more frequently found as a result of their application to the removal of oil spills. First, the extent to which dispersants are biodegraded, as an indication of their suitability for use on a large scale, is discussed. Biodegradation may be carried out by means of monocultures or mixed cultures of marine bacteria of the genera *Aeromonas, Pseudomonas,* and *Flavobacterium.* Analytical techniques based on absorbance measurements were used to follow the process. On the other hand, by determining the kinetics of the biodegradation process a more complete analysis is obtained. The kinetic coefficients controlling the process are deduced and it is shown that for some dispersants the experimental results are in close agreement with the proposed scheme. Where observed values are explained on the basis of ethylene oxides content of the dispersants, estimations of the amount of dispersant present in the sea at a given time can be made, if the amount of the dispersant first used is known.

Introduction

The continous impoverishment in oxygen both in waste and marine waters was soon related to industrial progress and the birth of detergents. The presence of detergents in the sea has been greatly increased due to their use in the treatment of oil spills. In order to carry out this treatment on a large scale with dispersants it is necessary to find out previously how they will affect the medium. Thus it is quite usual to carry out a study on the biodegradation of dispersants, which will allow a prediction of their level in the sea at any time.

Garret (1967) has pointed out the presence in the sea of surfactants and their residual products; the latter result, possibly, from the metabolization of the hydrophobic part of these compounds (Fischer and Gerike 1975).

Non-ionic dispersants have replaced ionic in certain fields, because of advantages such as their compatibility with many substances that react with and inactivate anionic and cationic agents (Cruickshank 1968; Bourrel et al. 1979), although they have not been greatly applied to the treatment of oil spills. Among the non-ionic dispersants an important group is the polyoxyethylene fatty acid esters, which result from the reaction of fatty acids C_{12} to C_{18} with sorbitol and a later addition of ethylene oxides. Due to the wide structural variety shown by this group of substances their study is very complex and although some authors (Fincher and Payne 1962) have related their biodegradation to the content of ethylene oxides, others disagree (Schick 1967).

In order to follow the biodegradation process with a certain facility compounds with oleic acid, thus having double bonds C=C, were first chosen. The theoretical degradation scheme of these compounds was discussed in a previous paper of this department (Bao and Bergueiro 1977). Our study was later extended to other surface active agents of the same or equivalent series.

The micro-organisms used were selected on the basis of reports by many authors who have carried out degradation of dispersants with cultures of *Pseudomonas* and *Flavobacterium* genera (Goodnow and Harrison 1972; Hsu 1965; Atlas and Bartha 1972). It is well known that micro-organisms adapt themselves to the medium, so that by isolating them in polluted areas, satisfactory results can be obtained. Thus for this investigation *Flavobacterium* and *Pseudomonas* together with *Aeromonas* genera were isolated from

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sea-water of the Galicia Estuaries after an oil spill.

As a further step in the work reported in this paper, the simultaneous biodegradation of the dispersants and petroleum in sea-water will be carried out.

Materials and Methods

Micro-organisms. Flavobacterium pictorum, Pseudomonas sp., and *Aeromonas sp.*, isolated from Galicia Estuaries, were used throughout this study. The first two belong to genera which easily degrade dispersants and the third one has been chosen because of its great abundance in the place where the samples were collected.

Substrate. The following non-ionic dispersants were used in sea-water in the following concentrations:
Span 65 = Sorbitan tristearate – 1 g/l.
Span 80 = Sorbitan monooleate – 5 g/l.
Tween 20 = Polyoxyethylen (20) sorbitan monolaurate – 5 g/l.
Tween 80 = Polyoxyethylen (20) sorbitan monooleate – 2 g/l.
Tween 85 = Polyoxyethylen (20) sorbitan trioleate – 1 g/l.
Corexit 7664 = Polyoxyethylen (13.5) glycerol trioleate – 2 g/l.

We have used a range of high concentrations because we think that there may be similar cases to those found in Galicia Estuaries (where the samples of water and micro-organisms have been taken) in which the concentrations of dispersants after an oil spill are higher than average. This can be explained as a result of the slow renewal and movement of water in the absence of naturally generated turbulence.

The dispersants of Span and Tween series, developed by Atlas Powder Co., were supplied by Comercial Química Massó (Barcelona, Spain). The Corexit was supplied by Esso Research and Engineering Co.

Sea-water from Galicia Estuaries was autoclaved (at 121° C for 15 min) before use.

Process Conditions. The pH is maintained between 7.5–7.8, a quite normal value in Galicia Estuaries. The bacteria are cultivated in a relatively poor PYM medium (1 g Peptone, 0.5 g yeast extract, 800 cm^3 sea-water, 200 cm^3 distilled water) keeping the flasks in a rotary shaker at 30° C until high growth occurred (30 h), and the viable cell count had risen to 10^9/ml. This culture was used to inoculate (in a quantity of 0.1 ml) the solutions of dispersants in sea-water; test tubes of 2.5 cm diameter filled up to one third of their capacity (30 ml) were used. Three test tubes were prepared for each measurement of absorbance: one with dispersant and inocule (experimental), other without dispersant and with inocule (blank) and a third one with dispersant and sterile medium (standard). The set of test tubes was incubated at 15° C and 150 rpm for a maximum of 25 days, during which measurements of absorbance are taken in a psychroterm incubator (New Brunswick Sci. Co). The samples were centrifugated at 5,000 rpm for 30 min and their degradation was determined by analytical techniques.

Analytical Methods. The APHA (American Public Health Association) method was used to determine the chemical oxygen demand (COD) whereas the API (American Petroleum Institute) method modified (Núñez 1982) was used to control the biochemical oxygen demand (BOD).

To follow biodegradation two methods were utilized:

Method 1. This method is based on the absorbance shown by the C=C group at 235 nm. The determined concentration corresponds to compounds with double bonds present in the dispersant and in its biodegradation products. In our case it is only valid for dispersants containing oleic acid.

Method 2. This method proposed by Clanet and Viller (1976) is based on the formation of a coloured complex with the salt of a heteropolyacid, such as ammonium cobaltothiocyanate, which is extracted from benzene. Its absorbance is measured at 320 nm (Pye Unicam 1700 Spectrophotometer).

This method is limited because the loss of the dispersant property and not necessarily the full degradation is measured. Our interest is, however, precisely the biodegradation which leads to the loss of that dispersant property, and thus the method is suitable.

Results and Discussion

A first group of dispersants has been chosen on the basis of their content in oleic acid, each one of which contains a different amount of ethylene oxides: Span 80 (0 mol), Tween 80 (20 mol), and Corexit 7664 (13.5 mol).

On the other hand, to select a second group of dispersants, the BOD and COD of a large number of compounds of the Span and Tween series were determined and we chose Span 65, Tween 20, and Tween 85 because they showed the lowest oxygen demand.

The selected micro-organisms were first tested in pure and mixed cultures on Tween 80, the *Aeromonas sp.* being found to be the most effective (Fig. 1). Thus it was used in the experiments with the other dispersants. The *Aeromonas* genus, although not usually studied as a degradator of surface-active agents, was found in large amounts in the place where the samples were collected and thus its high degrading capacity did not surprise us.

The results are summarized in Figs. 1–5. Figures 1–3 were obtained by following the biodegradation process using the analytical Method 1 applicable only to surface active agents that contain oleic acid. Figures 4 and 5 were obtained by applying the analytical Method 2 to all the tested dispersants. It can be assumed that all final degradation values (which are the same for each compounds, irrespective of the analytical method used) indicating that the degradation is in direct relation to the number of ethylene oxides of the molecule.

It must be pointed out that all figures are similar in showing a close resemblance to graphs of bacterial growth, indicating that this and biodegradation take place in a parallel way (Van der Kooij et al. 1982). In each figure a minimum degradation value is observed which arises at different times according to the genus of the bacterium; in some cases biodegradation

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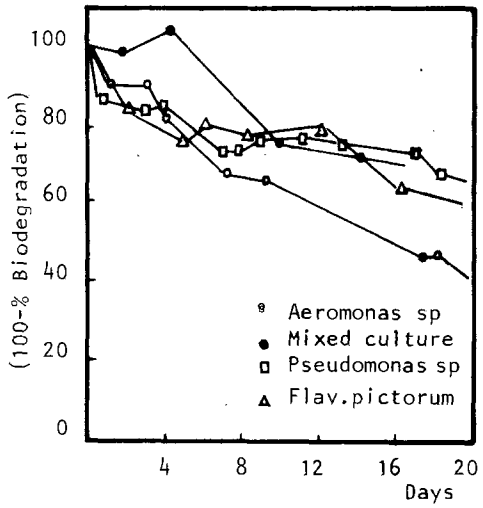


Fig. 1. Degradation of Tween 80 (Method 1) by means of pure cultures of *Aeromonas sp, Pseudomonas sp, Flavobacterium pictorum* and a mixed culture of these micro-organisms

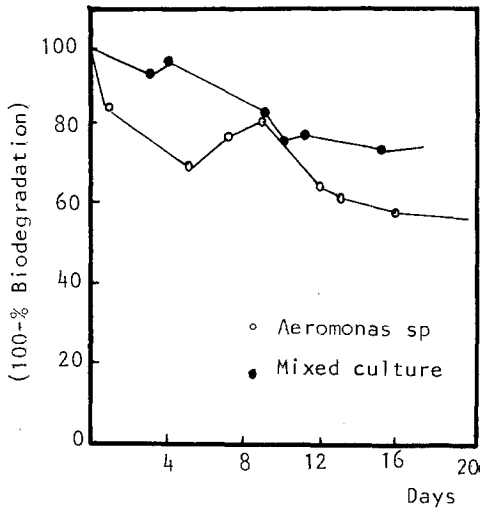


Fig. 2. Degradation kinetics of Corexit 7664 (Method 1) by means of a pure culture of *Aeromonas sp* and a mixed culture of *Aeromonas sp, Pseudomonas sp,* and *Flavobacterium pictorum*

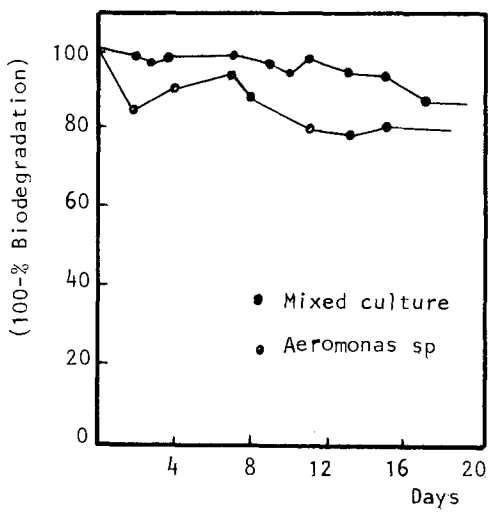


Fig. 3. Degradation kinetics of Span 80 (Method 1) by means of a pure culture of *Aeromonas sp* and a mixed culture of *Aeromonas sp, Pseudomonas sp*, and *Flavobacterium pictorum*

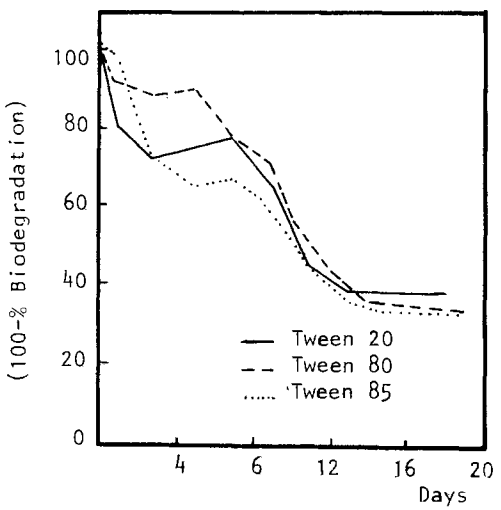


Fig. 4. Degradation kinetics (Method 2) of Tween 20, Tween 80, and Tween 85, by means of a pure culture of *Aeromonas sp*

appears to be reversed, and this can be interpreted as a release from the bacterial membrane of compounds analogous to the one being determined (Socatch 1969). From days 12 to 16 the degradation is almost constant, which indicates that bacterial activity tends to cease.

From Figs. 1–3 it is seen that the mixed culture does not have any advantage over pure cultures for dispersant biodegradation, an observation made previously by other several authors (Soli and Bens 1973). The Span 80 (Fig. 3) shows a very low degradation, which may either be because its concentration is close to the toxic level for bacteria, or because it has an excess in free oleic acid, a factor that has caused bacterial inhibition in similar cases (Rose et al. 1966).

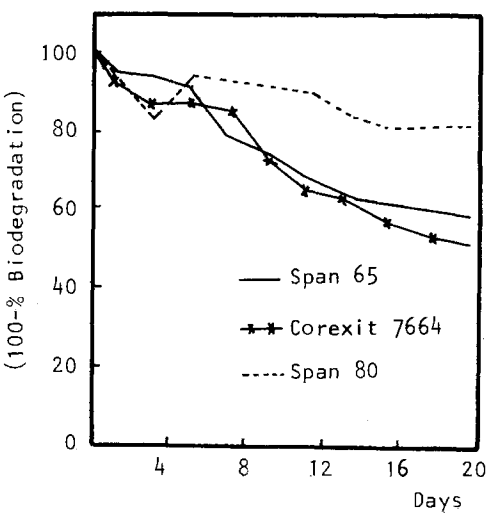
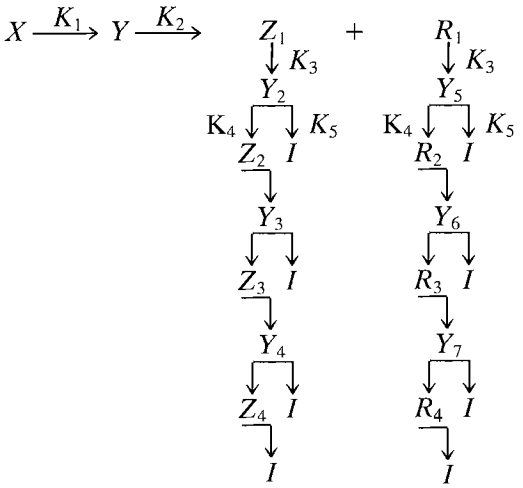


Fig. 5. Degradation kinetics (Method 2) of Span 65, Span 80, and Corexit 7664 by means of a pure culture of *Aeromonas sp.*

The results of degradation by *Aeromonas sp.* of the Span 80, Tween 80 and Corexit 7664, all containing oleic acid, have been compared and with the aim of elucidating the actual process, we set up a kinetic model based on β-oxidation theory (Stumpf 1969) on the following scheme:



where X represents each one of the dispersants containing oleic acid, Y is this acid, and Z_1 and R_1 are the nonanoic and azelaic acids, respectively. The compounds designated by Y are similar to oleic acid, that is, they contain C=C, while Z and R designate compounds with no C=C obtained in the different degradation steps. I is Ac-CoA (acetyl-Coenzyme A) which forms part of the respiratory chain of the bacteria.

Taking into account that reactions $Z \rightarrow Y$, $R \rightarrow Y$ are similar whatever their subindex may be, and considering that the kinetic coefficients for parallel reactions are also very similar, the number of significant coefficients to represent the process is limited to those shown in the scheme.

From the experimental results and using the model equations the kinetic coefficients are calculated. This is carried out by means of a technique (algorithm of the gradient) previously used in our department (Girondo 1975) based on the assumption that the deviation between the experimental value and the corresponding theoretical one is reduced to the minimum. From an assumed value of the coefficients, the algorithm improves the values by iterations according to the least square method in the direction of the maximum gradient. The results were obtained by means of a Fortran V computer program.

The values of the coefficients, summarized in Table 1, show a substantial agreement with the proposed scheme, where it is clear that the coefficients K_4 and K_5 must be equal since they belong to the same reaction. Thus, the values of each one of the kinetic rate coefficients K_3, K_4, and K_5 remain constant for the three tested dispersants, with K_4 almost equal to K_5.

Table 1. Results of the proposed degradative scheme

Dispersant	Span 80	Corexit 7664	Tween 80
Number of moles of E. O.	0	13.5	20
Kinetic coefficients (days^{-1})			
K_1	2.100	1.880	0.570
K_2	0.100	0.670	2.860
K_3	0.012	0.010	0.009
K_4	0.035	0.030	0.030
K_5	0.035	0.030	0.030

The kinetic coefficient K_1, which controls the step:

$$\underset{(X)}{\text{Dispersant}} \xrightarrow{K_1} \underset{(Y)}{\text{oleic acid}}$$

takes values completely different for the three dispersants, these values being higher the smaller the number of ethylene oxides. This can be explained as follows:

1. The enzyme is excited in the presence of polar points (Kieslich 1975).
2. The enyzme may go to the acid group and their interaction can be difficult due to steric hindrance in the presence of ethylene oxides.
3. It could happen that due to the formation of micelles, the concentration of substances containing ethylene oxides decreases.

The rate constant K_2, which controls the step:

$$\underset{(Y)}{\text{Oleic acid}} \xrightarrow{K_2} \underset{(Z_1)}{\text{nonanoic acid}} + \underset{(R_1)}{\text{azelaic acid}}$$

takes different values that are inverted with regard to the previous step and which are increased when the number of moles of ethylene oxides rises.

The most plausible explanation is that the enzyme takes an associated remainder that acts as an enzymatic activator. When the structures of dispersants are compared, it is understood that the activator derives from the ethylene oxide group. The remainder must be released in further steps and this release will explain the fact that the following kinetic coefficients have the same value.

From these results the amount of dispersant present in the sea at any given time can be predicted.

Acknowledgments. We would like to thank the Department of Microbiology of the Faculty of Pharmacy (Santiago de Compostela) for having supplied the micro-organisms and for the use of

ED_001324_00000573-00004

their equipment. We are very grateful indeed to Dr. Juan Luis Barja Pérez, a member of the staff of that department, for his continuous help. We are also grateful to Ldo. E. Patiño for his advice in the preparation of the manuscript in English.

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Received December 29, 1982

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To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Fri 7/24/2015 5:01:50 PM
Subject: dispersant inventory

Here is the list of dispersants in the laboratory with dates and quantities. I also marked the ones that I am using for the preliminary BFT testing.

Current Inventory of Oil Spill Dispersants Line Items (July 2015)

date	dispersant name	quantity in lab	in use for preliminary testing
Apr-95	Corexit 9500	~ 100 mL	
Jul-97	EC9527A	~ 150 mL	
19-Dec-01	Nokomis 3-F4	1 qt.	
Aug-06	Dispersit SPC1000	~600 mL	*
undated, before 2010	JD-2000	~ 20 mL	*
undated, before 2010	Saf-Ron Gold	~ 300 mL	*
undated, before 2010	SX-100	~ 100 mL	
undated, before 2010	Corexit 9500A	~ 40 mL	
18-Jun-10	Corexit 9500 from Ohmsett	< 50 mL	*
25-Jul-13	new dispersant gel sent to AI from Tim @ ExxonMobil	~ 20 mL	
Apr-14	Finasol OSR52	1 qt.	
19-Mar-15	Nokomis 3-AA	1 pt.	*
19-Mar-15	Nokomis 3-F4	1 pt.	
9-Apr-15	FFT Solution	1 qt.	
16-Apr-15	Accell Clean DWD	1 qt.	
6-May-15	ZI-400	1 qt.	*

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

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Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Mike Fulton - NOAA Federal
Sent: Tue 9/1/2015 7:10:04 PM
Subject: Re: dispersant

By the way, if possible I'd like to have a couple other folks sit in.
Mike

On Tue, Sep 1, 2015 at 3:00 PM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

Thanks Robyn. Sometime Thursday morning would work.
Mike

On Tue, Sep 1, 2015 at 12:10 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Mike,

Never a pest! I am tied up with meetings today and tomorrow. Would Thursday work for you?

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Robyn N. Conmy, Ph.D.

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727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Mike Fulton - NOAA Federal [mailto:mike.fulton@noaa.gov]
Sent: Tuesday, September 01, 2015 10:34 AM
To: Conmy, Robyn
Subject: Re: dispersant

Hi Robyn,

Sorry to be a pest, but it would be great if we could arrange to chat about dispersants, cleaners and bioremediation agents. Thanks.

Mike

On Wed, Aug 19, 2015 at 9:28 AM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:

> Hi Robyn,
>
> I hope you're well. Would you have some time in the next week or so to discuss our joint interest in dispersants, shoreline cleaners,and bioremediation agents? Thanks.
>
> Mike

> On Thu, Jul 30, 2015 at 2:04 PM, Mike Fulton - NOAA Federal <mike.fulton@noaa.gov> wrote:
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> > Hi Robyn,
> >
> > Is there a time next week when we could chat about sharing dispersants? Thanks.
> >
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Hi Robin,

We do have both. I suspect we have enough to share. I'll check and let you know early next week. One caveat...we'd have to the pull the material for you from a larger container. We didn't receive separate aliquots. Can that work?

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I couldn't recall if you said your lab has finasol and corexit in stock for testing? If so, would you have any to share with us? We are running low and trying secure a liter or 2 of each.

Thanks,

Robyn

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Utility of characterizing light attenuation within Northwest Florida Estuaries: implications for RESTORE Act water quality monitoring

Robyn N. Conmy[1*], Blake A. Schaeffer[2], Joseph Schubauer-Berigan[1], Jessica Aukamp[3], Allyn Duffy[3], John Lehrter[3], Richard Greene[3]

U.S. Environmental Protection Agency, Office of Research and Development
[1]NRMRL Land Remediation & Pollution Control Division, 26 W. MLK Drive, Cincinnati, OH 45268
[2]NERL Immediate Office, 109 T.W. Alexander Dr., Research Triangle Park, NC 27711
[3]NHEERL Gulf Ecology Division, 1 Sabine Island Drive, Gulf Breeze, FL 32561
[*]Corresponding author: conmy.robyn@epa.gov, (ph) 513-569-7090, (fax) 513-569-7620

Abstract

150 words

For more details on the RESORE Act and the Council go to restorethegulf.gov.

Target Journal: Marine Pollution Bulletin

Keywords: Deepwater Horizon Oil Spill, RESTORE Act, Northwest Florida Estuaries, Water Quality & Clarity, Light Attenuation

Introduction

The 2010 Gulf of Mexico (GoM) Deepwater Horizon spill (DWH) released ~800 million liters of Light Louisiana Sweet Crude Oil from 1500 m ocean depth. Seven million liters of chemical dispersant (Corexit© 9527 & 9500A) were applied to minimize surface oil slick formation and environmental impacts at the air-sea interface (budget calculator report, 2010). Although the point of release was > 75 km from the nearest coast and at a water depth of 1.5 m, the high volume and extended duration of the spill negatively impacted Gulf State communities and ecosystems (Ref). Affected were local economies, protected natural resources, ecological health and ecosystem services (Ref). During and following the spill, DWH oil residues were advected along GoM beaches, interacting with suspended sand and waves, forming submerged oil tar mats and surface residual oil tar balls. The presence of tar balls and mats continue to be a problem along Florida and Alabama beaches more than four years after the DWH spill, particularly after major storm events (Plant et al., 2013; Mulabagal et al., 2013; Hayworth et al., 2015).

To provide restitution to the Gulf Coast region, the Resources and Ecosystems Sustainability, Tourist Opportunities, and Revived Economies of the Gulf Coast Act of 2012 (RESTORE Act) was passed, which diverts 80% of civil and administrative Clean Water Act (CWA) penalties collected from the DWH spill to the Gulf Coast for ecological and economic restoration. The Gulf Coast Restoration Trust Fund was established, where monies are divvied up into five portions including (1) the Direct Component (35%, split equally to the five Gulf States: Alabama, Florida, Louisiana, Mississippi and Texas) to develop multi-year implementation plans; and (2) the Council-Selected Restoration Component (30% allocated to the Gulf Coast Ecosystem Restoration Council) to develop and implement the Comprehensive Plan (Plan, August 2013). In 2014, a total of 50 project proposals were submitted to the Council by the States and Federal Agencies.

The Council has adopted 5 RESTORE goals: restore and conserve habitat, restore water quality, restore and revitalize the Gulf economy, replenish and protect living coastal and marine resources, and enhance community resilience. Nearly all of the submitted proposals list restoring water quality as either a primary or secondary goal (ref proposal summary pdf), where watershed restoration is a common denominator. Yet few mention the suite of measurements that will be targeted to assess a holistic view of water quality. Discussion on water clarity, or the presence of chlorophyll, color and turbidity as contributors to water quality is non-existent in 90% of the proposals. In order to accomplish proposal goals, however, assessment of water clarity is critical.

Light attenuation, or water clarity, within natural water bodies is central to the health and

function of ecosystems. Many biogeochemical processes are predicated quite simply on the number of photons and the spectral makeup of light filtering through a water column. Clarity is influenced by scatters and absorbers of light, such as phytoplankton, colored dissolved organic matter (CDOM, or color) and non-algal particles (NAP) (refs). In open ocean waters, the interplay of attenuators is often simplistic where phytoplankton is the dominant attenuator and contribution (and variability) of remaining attenuators is minimal (refs). Hence, predicting light attenuation is often less challenging in these waters. Measurements typically focus on the inherent optical properties (IOPs): absorption (a) and scattering (b) coefficients; and apparent optical properties (AOPs), such as the diffuse attenuation (K_d) coefficient. The former are a function of components within the water alone (Kirk, 1994), are additive, linear, and proportional to concentration. The sum of absorption coefficients due to water (a_w), detritus or NAP (a_d), CDOM (a_g) and phytoplankton (a_ϕ) equal total absorption (a_t) as shown in eqn. 1.

$$a_t(\lambda) = a_w(\lambda) + a_d(\lambda) + a_g(\lambda) + a_\phi(\lambda) \qquad (1)$$

AOPs, however, are not additive and depend not only on constituents within the water but also on the ambient underwater light field, influenced by surface waves, sun angle, depth and cloud cover (Morel & Smith 1982). The diffuse attenuation coefficient, $K_d(\lambda)$, describes the loss of light through the water column as defined by eqn. 2, where $E_d(\lambda)$ is spectral solar downward irradiance over depth (Preisendorfer, 1976). IOP and AOP coefficients can be defined at specific wavelengths, (λ), or integrated over pertinent ranges, such as PAR (Photosynthetically Active Radiation, 400-700 nm) (Mobley, 1994; Anastasiou, 2009), but are typically reported at single wavelengths in offshore waters.

$$K_d(\lambda) = \ln [E_d(z,\lambda) / E_s(z,\lambda)] \qquad (2)$$

In coastal waters, however, generalizations about optical properties are impeded by the inherent variability and complex physical / biogeochemical nature of these environments, resulting in region-specific trends (Duarte, Gallegos, Babin, Kelbe, Anastasiou, etc). In estuaries, the presence of attenuators influences the amount of light available to seagrasses and benthic algae (Kirk, 1994), pollutant fate and nutrient cycling (ref). Terrestrial environments are a significant source of CDOM, detritus and NAP in these systems; where distribution can be correlated with river discharge, precipitation, temperature and extreme weather events (Eimers et al., 2008). Anthropogenic land alteration and nutrient loading also impact fluxes of attenuators (Bauer et al., 2013). Beyond ecosystem health, clarity is tied to local economies, where the aesthetics of water bodies influence tourism, fisheries and housing (ref). Thus much effort has been dedicated to the characterization of light-attenuating constituents and their role in water quality.

In estuaries the bulk of light attenuation-relevant measurements are collected via resource managers for establishing and monitoring water quality targets. In the 2008 US EPA National Coastal Condition Report III, development of water quality indices was based on component indicators including chlorophyll *a* and water clarity. Clarity ratings were based on (1) natural variations in turbidity levels, (2) expectations for light penetration related to submerged aquatic vegetation (SAV) distribution and (3) local waterbody management goals. The report highlights that at the core of management practices, PAR impairment is predicated on suspended and dissolved materials within water (refs). Though to evaluate this, IOPs (absorption or scattering) are often not measured, but rather quasi-IOPs (chlorophyll *a*, color, total suspended sediments (TSS) and turbidity) are collected (Anastasiou, 2009). Their concentration, in many cases, can be correlated with magnitude of IOP coefficients but are not mathematically applied to any equations defining K_d. Hence, water quality targets are reliant on AOP-related measures (PAR, percent surface irradiance, secchi depth) and quasi-IOPs, but with no direct quantitative link between them. This approach can be problematic as initiation of management actions require not only documenting changes in light attenuation, but also identifying and quantifying the root causes of light limitation (Anastasiou, 2009; Fitzhugh, ??; Schaeffer et al., 2012). Characterizing both would help to establish thresholds and impairment, and with estuarine monitoring.

Characterizing water quality and clarity (WQC) metrics is also important for RESTORE Act projects where assessment of existing watershed and coastal baseline data is required. Approaches that correlate inherent, apparent and quasi-optical properties are critical for project success where an assortment of mined data will be used in comparative analyses of watershed, loadings and land use alterations. Such is the case for the nine RESTORE proposals targeting Florida waters, where 88% cite restoring water quality as a primary goal. The under-sampled, contrasting estuarine systems of Northwest Florida: Pensacola, Choctawhatchee, St. Andrew and St. Joe Bays are targeted estuaries within these proposals. Reported here are absorption coefficients, quasi-IOPs and diffuse attenuation of these systems collected prior to, during and after the DWH oil spill. **This paper aims to (1) describe light absorption in surface waters of four NW Florida estuaries, (2) determine the relationship of absorption coefficients at 412 nm and integrated over PAR and (3) establish the total absorption coefficient (a_{t-w}) as a valuable management parameter that can be quantitatively linked to the concentration of attenuating materials within these systems.** Results offer a means for researchers and managers to translate and utilize data routinely collected by one another, thereby closing data gaps within temporo-spatially coarse coastal monitoring programs. Such approaches are valuable for future monitoring, as these parameters can be supplemented with space-based satellite estimates allowing for long-term, low-cost high resolution monitoring (Schaeffer et al., 2015) and measured from in situ sensors commonly used in oil spill detection (Conmy et al.,

2014). Benefits of our work to the RESTORE proposals is three-fold. Findings can guide sampling and monitoring designs, serve as baselines for watershed restoration efforts, and provide for resiliency and oil spill preparedness within Florida waters.

Methods

Water samples and in situ measurements were collected during boat-based surveys within Pensacola, Choctawhatchee, St Andrew and St Joe Bays between September 2009 and November 2011 (Figure 1). All methods follow a U.S. Environmental Protection Agency level II QAPP (Quality Assurance Procedural Plan) and standard operating procedures.

Setting - The Northwest Florida coast of the United States comprises the 'forgotten' and 'emerald' coasts which includes four large estuarine systems: Pensacola, Choctawhatchee, St Andrew and St Joe Bays (Figure 1). The coastal waters in this region retain a score of 'good-fair condition' on the Gulf Coast Water Quality Index (EPA Report, 2008). Land development Index scores (Vivas and Brown, 1995?) for the watersheds are all low (< 2), where land use is dominated by forest and wetlands. Yet, residing counties of these estuaries exhibit population growth rates between 5-33%, which are some of the highest in the state (US Census Bureau, 2000). High rates of development coupled with the regional unimpaired water status validates the need to evaluate light attenuation and potential stressors that could threaten or impact natural attributes of these coastal systems.

Estuaries were chosen in part due to their contrasting features. Two are river-fed systems: Pensacola Bay is a large, lobed system that is supplied by three main rivers and Choctawhatchee has one main river (3rd largest in the state) that feeds the top of the estuary. Mean annual freshwater discharge of the former is 324 m^3s^{-1} (Bianchi et al., 1999) and 204 m^3s^{-1} (Kenner et al., 1971) of the latter. These systems also possess large watershed areas, 18,125 km^2 and 13,835 km^2 for Pensacola and Choctawhatchee Bays, respectively. Figure 2 illustrates the discharge regime for the Escambia (Pensacola Bay) and Choctawhatchee Rivers during the study sampling period, where there is large interannual variability and maximum discharge occurring in winter / spring months.

Conversely, fresh water delivery to St Andrew and St Joe Bays is substantially lower. St Andrew Bay is supplied by a series of small creeks that drain to Deer Point Lake Reservoir before discharging to the estuary. The base flow for these creeks is high because they are sourced from spring networks of the Floridan Aquifer. Ecofina Creek for example has a base flow of 16 m^3s^{-1} (Brown, 2009). Compared to the other NW Florida systems, St Joe is supplied by a small canal. The limited freshwater makes this system a coastal lagoon even though it is referred to as a bay.

In situ / Electronic Sampling - Hydrographic profiling measurements were collected using a Seabird CTD package. Given that northwest Florida estuaries are very shallow with abrupt vertical gradients, the CTD was deployed sideways and lowered slowly at a rate of approximately 10 cm s^{-1}. The CTD profiling package provides for measures of water column temperature, salinity, density, dissolved oxygen, depth, turbidity, light attenuation, and chlorophyll and CDOM fluorescence (WetLabs, Inc sensors). Data processing follows manufacturer recommended procedures and binned at XXX. (ref needed). Secchi depth measurements were also collected at each estuarine station and reported in per meter. Data processing methods needed.

A hyperspectral profiling system (Satlantic HyperPRO) was deployed for hyperspectral radiometric (HyperOCR) measurements (350-800 nm, resolution 5 nm) of upwelling and downwelling water radiance. The Hyperpro supplies E_d, downwelling cosine-weighted irradiance, data at all depths. The coefficient K_dPAR characterizes the averaged (over a water column) vertical decrease in natural light in the PAR. For these calculations irradiance values were plotted against depth (for the 0.1–3 m layer) and K_dPAR was found as the exponent of the least-squares regression line through these point. (Paavel et al, 2011). Procedures for HyperPRO profiling are based on methods detailed in National Aeronautics and Space Administration Ocean Optics Protocols for Satellite Ocean Color Sensor Validation (Mueller, 2000).

Discrete Sampling - Water samples were collected 0.5 m below the air-water surface (referred to as surface) for absorption (chlorophyll, non-algal particulates, CDOM) and extracted chlorophyll analyses. Water was kept on ice and in the dark and then transited to the laboratory for analyte preparation.

Spectroscopic Analyses - Using polypropylene gloves, water was filtered through Whatman 47 mm GF/F filters (nominal pore size = 0.7 μm) into combusted glass flasks for CDOM analysis. CDOM absorption was measured in a 1 cm cuvette using a Shimadzu UV1700 dual-beam spectrophotometer at 1 nm intervals between 200-700 nm with Milli-Q deionized water as a reference. Spectra were normalized by subtracting from each wavelength the measured value at 700 nm (Pegau et al., 2003), CDOM absorption coefficient $a_g(\lambda)$ and spectral slopes (S) were calculated following (ref). Water samples were analyzed for absorption by total particulates on Whatman 25 mm GF/F filters with a Shimadzu UV1700 dual-beam spectrophotometer at 1 nm intervals between 400-800 nm with 0.2 μm filtered seawater as the reference using the quantitative filter pad technique (Pegau et al., 2003). Pigments were extracted from filters with warm methanol and rescanned to measure the detritus absorption (Kishino et al., 1985). Phytoplankton absorption coefficients $a_{ph}(\lambda)$ were calculated as the difference between total

particulate absorption and detritus absorption $a_d(\lambda)$. Spectra were corrected for baseline noise by subtracting each wavelength from the mean measured value between 790-800 nm (Pegau et al., 2003). Data processing / integration methods needed.

Extracted chlorophyll – Water samples for chlorophyll were filtered onto a 25 mm Whatman GF/F filter (nominal pore size 0.7 µm), and the filters immediately frozen at -20°C or colder in a 50 ml polypropylene centrifuge tube and water volume filtered was recorded. Method and Ref Needed.

Results and Discussion

Since the 19th century, secchi depth, Z_{SD}, has been used as an indicator of water clarity (Preisendorfer, 1986). Although inexpensive and easy-to-use, measurements are flawed by observer subjectivity, disc variability, above-water light conditions, and by coarse 0.25 m sampling intervals (Davies-Colley and Smith, 2001). For NW Florida estuaries, the diffuse attenuation coefficient, K_dPAR, is inversely related to Z_{SD} where largest variability occurs in waters with decreased transparency or shallower Z_{SD} (Figure 3). Secchi depth ranged between 0.4 and 8 m^{-1}, with highest values observed in St. Andrew Bay in January 2010, at a station nearest the estuary mouth (#7). K_dPAR ranged between 0.08 and 0.98 m^{-1}, where large ranges in K_dPAR exist for a given Z_{SD}. For example, at a Z_{SD} of 2m, K_dPAR can range from 0.13 - 0.46 m^{-1}, or a 63 % difference, thus illustrating the limitations and/or complications of Z_{SD} as a quantitative index. Furthermore, secchi is limited by its depth range, both for very shallow, but optically clearer waters, and for deeper waters that test the depth limits of the disc.

Salinity ranged between 0 and 35.14 for Pensacola, Choctawhatchee and St. Andrew estuaries, and a narrower range of 21 and 34.25 for St. Joe which receives the least amount of terrestrial runoff (Supplemental Table 1). CDOM and detritus absorption coefficients (a_g412 and a_d412) are inversely proportional to salinity and driven largely by freshwater input for the systems sampled (Figure 4). Majority of a_g412 values in Pensacola, Choctawhatchee and St. Andrew bays ranged between 0.1 – 12 m^{-1}, with a few values above 14 m^{-1} for near zero salinity waters, and the largest value at 17.2 m^{-1} in Choctawhatchee Bay (station 10) in May 2010 after a large rain event. St. Joe exhibited the least colored water with a_g412 values of 0.1 - 3.9 m^{-1}. In all systems, the relative of contribution of detritus is smaller compared to that of CDOM, where a_d412 values ranged between 0.02 – 6.9 m^{-1}, and lowest values observed in St. Joe Bay. For some high salinity waters, elevated a_g412 and a_d412 values were found. This is easily observed for Choctawhatchee Bay samples from July and September 2011. Previous studies have demonstrated a reversal of the CDOM- salinity relationship at high salinities, attributed to concentration of material due to evaporation or new production of marine CDOM (Conmy et al 2010; Coble). This may have been the case here, as river discharge was the lowest recorded,

warm summer conditions prevailed, and stations are in shallow water with productive sediments (St. 7,8,9), but is difficult to discern the cause here.

In addition to CDOM magnitude variability, the spectral quality of the absorption coefficient varies within estuaries, as evident from the spectral slope ($S_{280\text{-}312nm}$ and $S_{350\text{-}412nm}$) values (Figure 5). Higher a_g412 values correspond to lower $S_{280\text{-}312nm}$ (Figure 5 inset) and represent riverine sources of CDOM with high lignin content (Helms et al 2008; Fichot and Benner, 2012). As material moves through the estuarine systems, CDOM concentration decreases and spectral slope increases due to photochemical transformations and aging, where greater loss of chromophores at longer wavelengths occurs relative to shorter wavelengths. $S_{280\text{-}312nm}$ values ranged between 0.0118 – 0.0287 m^{-1}, however the highest a_g412 values in St. Andrew Bay did not exhibit the lowest slopes. These stations are in located in the eastern lobe (East Bay) which drains a smaller, less forested watershed compared to Choctawhatchee and Pensacola Bays with lower slopes. This suggests material with slightly lower lability existed in the eastern portion of St. Andrew Bay. Examining slopes at longer wavelengths, $S_{350\text{-}412nm}$ reveals a similar relationship, but with a reversal of trend for select stations within St. Joe and St. Andrew Bays. Low $S_{350\text{-}412nm}$ (0.008 – 0.014 m^{-1}) and low a_g412 indicate an alternate, less refractory source of CDOM. Previous studies have reported on seagrass-derived (Zepp Burdidge, Stabenau) or phytoplankton-derived production (McKnight) of CDOM which were discerned by lower slopes. Our data implies that a source other than aged terrigenous material was present, likely seagrass beds or productive sediments below the sampled stations. Alterations to watershed and climatic shifts can influence not only the amount of DOM entering a system, but the chemistry as well (DOM ref and Salisbury).

Alterations to watershed and climatic events can influence the relative contribution of attenuators within coastal systems. On average, absorption due to chlorophyll was found to be low and the least dominant contributor to total absorption as evidenced by ternary diagrams (Figure 6). Chlorophyll had the largest percentage in St. Joe Bay during periods of lowest freshwater inputs in 2011. Conversely, CDOM is typically the largest contributor in all bays. Median %chlorophyll, %detritus and %CDOM values are 9%; 28%; 62% in Pensacola; 9%; 24%; 69% in Choctawhatchee; 4%; 14%; 80% in St Andrew; and 11%; 21%; 66% in St. Joe Bays, respectively. During times of resuspension or rain events, the contribution of detritus increases, but typically remains second to that of CDOM.

Given that the dissolved materials are the largest fraction, in these systems, absorbers and not scatters (particles) are.....Need to add something about using absorption and not scattering because interested in chl, CDOM and NAP. All three are absorbers, but only CDOM does not scatter (refs).

Figure 7 shows the correlation between a_g, a_d, a_{phi} for 412 nm and PAR integrated (a_xPAR). Whether Absorption coefficients calculated

TSS, chl, color vs absorption 412
Absorption coefficients were calculated at 412 nm and PAR-integrated for CDOM, detrital matter and phytoplankton for all bays. The two are tightly correlated, but aphi have largest variability, but still r2= ____. PAR range and ecological significance discussion here. Questions about which wavelengths are most appropriate.

Figure 8 shows the log transformed plots for relationship of quasi-IOPs to IOPs. Ad and ag are well correlated to turbidity and FDOM, respectively. This has been demonstrate din many other systems. Ag can also be correlated with color (Gallegos) with high degree fo accuracy. Chl, however, is not well correlated with aphi.

Albeit

Trophic State Index for lakes in Florida based upon secchi depth, chlorophyll and total phosphorous?

State where QAQC'd data can be found (EPA Access database). Should we have table of variables in the supplemental (like an appendix)?

It also establishes the applicability of IOPs for PAR-centric water quality standards.

PUT IN DISCUSSION For our systems we used the approach of only abs-tot b/c simplistic an dominant attenuator is CDOM, with does not scatter, followed by detritus which does both and then low chl which is high scatterer.

Also the use of fluorometers and particle meters will provide baselines for sensors used in spill response (Conmy et al., 2014)

Kelble paper findings.

Absorption coefficients found by ax(nm) = ax*(nm)[x], (but not ag b/c no concentration of color,

so use a440 directly).

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To: Bryan, Elisha[Bryan.Elisha@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Holder, Edith
Sent: Mon 4/20/2015 4:11:32 PM
Subject: RE: ZI-400 sample inquiry

Elisha,

Regarding Mr. Zelman's question about the NCP listing, Robyn will have to answer.

Robyn,

I have submitted a purchase order for ZI400 through Pegasus.

Edie

Edith Holder

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-569-7178

Email: holder.edith@epa.gov

From: Bryan, Elisha
Sent: Monday, April 20, 2015 8:49 AM
To: Holder, Edith
Cc: Conmy, Robyn
Subject: Fw: ZI-400 sample inquiry

Hello Edie & Robyn,

I am forwarding this message from ZI Chemicals. I could email him back and tell him that a different group covers those decisions and to send all questions to the contact listed in the link. I wanted to double check with both of you first.

I am not sure how you want to handle purchasing either.

Thanks,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Barnaby Zelman <zichemicals@mac.com>
Sent: Friday, April 17, 2015 8:29 PM
To: Bryan, Elisha
Cc: inquiry@ZIChemicals.com
Subject: Re: ZI-400 sample inquiry

Dear Elisha,

The cost, including UPS Ground service delivery of a 1 quart sample of our ZI-400 Oil Spill Dispersant made to order for the EPA would be $85. If this is acceptable please advise if you can issue payment via ACH, Wire transfer, or check (our last preference)?

May I ask one question...I could not find after cursory review of the link you provided where it mentions how long of a transition period would be allowed [after rule adoption] for manufacturers such as us to develop, test, submit, and list, the new products we will need to comply with the proposed revisions? For what it's worth, for us, we would like 2-3 years to be able to get any new products on the EPA listing before our existing product is removed. It's a matter of financial survival for small businesses such as ours and we do hope the EPA remains sensitive to this as well, given your own report indicated that 90% of current listed products are made by small businesses.

Thank you very much and awaiting your reply soonest.

Best regards,

Barnaby Zelman
Z.I. Chemicals
zichemicals@mac.com

On Apr 16, 2015, at 12:43 PM, "Bryan, Elisha" <Bryan.Elisha@epa.gov> wrote:

> Good Afternoon,
>
> The U.S. Environmental Protection Agency will be conducting a series of Dispersant Efficacy experiments using the newly proposed Baffled Flask Test for inclusion in the 40 CFR Appendix C to Part 300 Subpart J. I am a contractor with EPA's Office of Research and Development, National Risk Management Research Laboratory (NRMRL), Land Remediation and Pollution Control Division (LRPCD), working on this research.
>
> As your product is listed on the U.S. EPA National Contingency Plan Product Schedule, we would like to include your product in our research and are interested in procuring a small quantity. I am contacting all manufacturers listed so that we can take into consideration the different characteristics of the dispersants.
>
> This research will not change the current status of your product on the Product Schedule. More information on the proposed revisions and who to contact for comments can be found here: https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan#h-44.
>
> Could you please send me a price quote for one liter / quart of *ZI-400*?
>
> Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

POTENTIAL EFFECTIVENESS OF DISPERSANT USE IN THE U.S. BEAUFORT AND CHUKCHI SEAS

for:

Bureau of Safety and Environmental Enforcement
U.S. Department of the Interior
381 Elden Street
Herndon, VA 20170

by:

S.L. Ross Environmental Research Ltd.
200-1140 Morrison Drive
Ottawa, ON
K2H 8S9

December, 2014

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SLR
SL ROSS

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Disclaimer

This draft final report has not been reviewed by the Bureau of Safety and Environmental Enforcement (BSEE), nor has it been approved for publication. Approval, when given, does not signify that the contents necessarily reflect the views and policies of the BSEE, nor does mention of the trade names or commercial products constitute endorsement or recommendation for use.

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Executive Summary

The objective of the study has been to provide information to support dispersant use decision-making with respect to oil spill chemical dispersant effectiveness under the environmental conditions likely to be encountered in the U.S. Beaufort and Chukchi Seas.

The goals of the goals research were to:

1. Identify the prevailing environmental conditions in the U.S. Beaufort and Chukchi Seas that would affect dispersant performance (see Section 4 of this report);
2. Identify existing dispersant effectiveness tests that have been completed on Alaskan oils under conditions similar to those that exist in these two regions and identify gaps in the knowledge of dispersant effectiveness (see Section 5 of this report);
3. Conduct dispersant effectiveness tests at medium scale to address the knowledge gaps (see Section 7 of this report);

The primary environmental factors that have been shown to influence dispersant effectiveness include: wave energy; water salinity; water temperature; and presence and concentration of ice.

With the exception of isolated near shore fresh water outlets there is minimal variation (between 28 to 34 ppt (parts per thousand)), both temporally and spatially, in surface water salinity throughout the U.S. Chukchi and Beaufort Sea regions, at least from a chemical dispersant effectiveness standpoint. The performance of most chemical dispersants is generally not affected by salinity in the range of 25 to 35 ppt. Water salinities in the nearshore area of the Beaufort and Chukchi Seas can be considerably lower than the offshore areas for short periods of the year due to the influence of fresh water river outflows and ice melt. Fresh water from river outflow can form a 1 to 2 m deep lens under the landfast ice that may extend up to 25 km offshore from the major river mouths. The surface water salinities in these areas approach that of fresh water during the early ice breakup period and prior to the mixing of the upper and lower water layers by strong winds and waves. The presence of this near shore fresh water during this period could hinder the effectiveness of chemical dispersants.

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The surface water temperatures in the Chukchi and Beaufort Seas in the open water seasons can vary from close to freezing (-2 °C) to upwards of 10 °C. The chemical dispersibility of crude oil is affected by the temperature only as it affects the viscosity of the oil. The oil's viscosity is affected by the water temperature on which it sits and during sunny days by the heating of the surface of the oil by the sun. Different crude oils can have very different viscosities at the same temperature and many can be quite fluid at temperatures near freezing. There is really no water temperature that will completely restrict the use of chemical dispersant. The oil viscosity – temperature relationship must be considered for each oil before an evaluation of the potential for dispersant effectiveness can be made.

The presence of greater than 9/10ths ice cover eliminates the possibility of using conventional surface applied dispersant operations. The presence of the ice either encapsulates the oil making it impossible to target with aerial applied dispersant or dampens the surface energy such that there is insufficient energy to break the oil into droplets once treated. In ice conditions with less than 3/10ths cover chemical dispersants will perform much the same as in open water conditions since the surface mixing energy is not overly dampened by the presence of the ice. The performance of dispersants in 3/10ths to 8/10ths ice cover without additional mixing energy applied is somewhat uncertain. Research suggests that performance may be enhanced in these conditions by the energy generated at the ice edge as the ice pieces jostle even under low wave energy. In the Chukchi Sea region open water periods can exist in the months from June through November depending on the year. Open water is most common in the months of July through October in this region but the shoulder months of June and November may present dispersant application opportunities depending on the ice year. In the Beaufort Sea region the maximum likely extent for open water dispersant use is from July to October with the more likely season being from August to October.

Long term historical wave height data is not available in the U.S. Chukchi and Beaufort Sea regions for statistical assessment of the potential for successful dispersant use on a broad geographic scale. Long term wind data are, however, available for the region in the form of offshore hindcast wind data sets. Wave heights based on the Beaufort wind scale have been derived from hindcast wind speed data for this project. The percentage of time that wave heights

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favorable for chemical dispersant use exist in the US Beaufort and Chukchi Seas has been determined based on an assessment of 30 years of hindcast wind data from 5 stations located across the study area. For the open water months of July through October wave conditions favourable for chemical dispersant use exist across both regions from 71 to 91% of the time. These assessments do not take into account other variables such as visibility or daylight.

A review of scientific literature on the results of chemical dispersant effectiveness tests specifically conducted on Alaskan crude oils has been undertaken. Research that investigated chemical dispersant effectiveness under arctic conditions and in the presence of ice using other oil types has also been included in the review due to paucity of research in this area. The review has focused on the parameters that could affect dispersant performance that are of specific concern to the arctic environment. These parameters include the test temperature, the water salinity, the mixing energy and the presence of ice. Oil type, dispersant type and dispersant dosage have also been considered in this review. With a few exceptions, only tests that have used Alaskan oil have been reviewed. Only 10 of the 48 test programs reviewed studied dispersion in the presence of ice and only 7 of these varied the ice concentration in the test matrix and only two used Alaskan oil in the testing. Of the 48 studies reviewed, temperature was varied in 15, salinity was varied in 16, and mixing energy was varied in 29.

At the present time the only oils being produced and transported (by pipeline to shore) in the Beaufort and Chukchi Seas are Northstar and Endicott crude oils and are the only crude oils that could be spilled directly into Alaskan offshore waters from present production fields. No oils are presently being produced in Chukchi Sea waters. Alaska North Slope Crude (ANS), or Prudhoe Bay crude as it was named in early test programs, has been the Alaskan oil of choice for most of the dispersant effectiveness tests conducted on Alaskan oils. This oil is the pipeline blend that is transported to Valdez via the Trans-Alaska Pipeline. Only five of the test programs reviewed evaluated dispersant effectiveness on specific North Slope production crudes (Endicott, Northstar and Pt. McIntyre). These oils were used in projects that were conducted for the US Department of the Interior with oils sourced by them specifically for cold water dispersant effectiveness testing. These oils are possibly more representative of the type of crude that might be spilled in the Beaufort and Chukchi Seas. As new oils come into production in the waters of

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the Beaufort and Chukchi Seas they should be evaluated for their potential for chemical dispersion under the range of environmental conditions they might be spilled in.

Most of the past dispersant effectiveness tests on Alaskan oils used one or both of Corexit 9500 and Corexit 9527 in their testing.

There is concern in temperate or subarctic climates that temperature is a problem in dispersant effectiveness and that dispersants should not or cannot be used in cold climates. This concern is generally unfounded based on the research results, except in the case of so-called "high pour point oils", some of which can become semi-solid at temperatures well above freezing. Reduced temperature simply increases the viscosity of the spilled oil. The viscosity of the oil at the water temperature in which it is spilled is the key factor in deciding dispersant effectiveness and not the temperature per se. This points to the need to fully understand the properties of the specific oils that are likely to spilled in cold waters.

Numerous laboratory-scale, meso-scale and field studies, dating back to the late seventies, have been conducted to study the effect of water salinity on the effectiveness of oil spill chemical dispersants on a range of oils. The consistent significant finding of all of these tests is that dispersant designed for use in marine environments (30 to 35 ppt water salinity) are considerably less effective when the water salinity falls below about 20 ppt or above 40 ppt. Of the dispersants most commonly used in US waters, Corexit 9500 has been shown to be more effective than Corexit 9527 in lower salinity waters. Dispersants have been formulated for use in fresh water and these have also been tested for effectiveness over a range of water salinities, although not as extensively as the marine dispersants. The effectiveness of the freshwater dispersants have been shown to generally be much better than the marine products in freshwater but often achieve their best results in waters between 10 and 20 ppt salinity. The effectiveness of dispersants on the Alaskan oil under varying water salinities generally is consistent with the findings for other crude oils in these historical studies.

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Tests conducted in the past few years using the more energetic US EPA baffled flask test have indicated that the effect of salinity on dispersant effectiveness may not be as significant as identified in the earlier work. This may be due to the higher mixing energy imparted in this test.

After considering the above factors and discussion with a technical representative from the Bureau of Safety and Environmental Enforcement (BSEE), a suite of dispersant effectiveness tests using the SL Ross meso-scale wind-wave tank on four Alaskan crude oils with four water salinities were selected for additional study to shed more light on the effectiveness of marine dispersants over a range of water salinities under high energy breaking wave conditions.

Alaska North Slope, Endicott, Northstar and Kuparuk crude oil were used in the testing. Tests were conducted on fresh, evaporated and evaporated plus emulsified crude oils (3 weathered states in total). Northstar does not form a stable emulsion so tests could not be conducted on emulsions of this oil. Tests were conducted in water with salinities of 5, 10, 20 and 30 ppt. All tests were conducted with a water temperature of 10 °C. Corexit 9500 was applied at a dispersant to oil ratio of 1:20 in all tests.

The oil collected from the surface containment zone at the end of each test was compared to the volume of oil initially released to determine the quantity of oil removed from the surface during the test or the raw dispersant effectiveness (DE_{raw}).The DE_{raw} estimates have been adjusted by multiplying them by the volume fraction of oil present in drops smaller than 70 microns to arrive at a final dispersant effectiveness estimate that is referred to as DE_{70} throughout the report. The 70 micron drop size value has been reported as being the maximum oil drop size that will be permanently dispersed based on a series of field tests.

The fresh oils were more effectively dispersed than the weathered oils that were more effectively dispersed than the weathered and emulsified oils. The most complete data sets collected (due to limitations of the LISST in measuring large oil drops) were for the fresh oil tests. The results for the fresh oils indicate that the DE_{70} values are highest for the 30 ppt water and in all cases drop linearly as the test water salinity decreased to 5 ppt. The Northstar crude was most easily dispersed with complete dispersion (> 95% DE_{70} in 20 ppt salt water), followed by fresh ANS

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(95% DE_{70} in 30 ppt salt water), fresh Kuparuk (85% DE_{70} in 30 ppt salt water) and Endicott (40% DE_{70} in 30 ppt salt water). The DE_{70} dropped linearly to a value between 15 to 25 % for the oils tested as the water salinity decreased to 5 ppt. Similar linear trends in DE_{70} reduction with decreasing water salinity were identified in the weathered oil tests.

The highest DE_{70} recorded for any of the emulsified oils was 20% in 30 ppt salt water.

Even under the high energy breaking wave conditions used in this test program it would appear that water salinity had a significant effect on the ability of Corexit 9500 dispersant to assist in the generation of small oil drops that would likely be permanently dispersed in an ocean setting. The effect noted was the linear decrease in the volume of oil drops generated with small enough size to be considered permanently dispersed as the water salinity decreased from 30 ppt to 5 ppt.

The oil drops in some of the tests were visibly larger than the upper measurement limit of the LISST device used to measure oil drop size distributions and reliable drop size data could not be gathered for these tests. Development of an in-situ oil drop measurement system capable of cost-effectively measuring drop sizes in the 10 to 3000 micron range would improve the state-of-the art in oil dispersion monitoring both in large tank and field test conditions.

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Chemical Dispersant Research: Dispersant Effectiveness Testing at Ohmsett Using Aircraft Application Dosages

1 Objectives

The objective of the study has been to provide information to support dispersant use decision-making with respect to dispersant effectiveness under the environmental conditions likely to be encountered in the U.S. Beaufort and Chukchi Seas.

2 Goals

The goals of the proposed research were to:

4. Identify the prevailing environmental conditions in the U.S. Beaufort and Chukchi Seas that would affect dispersant performance (see Section 4 of this report);
5. Identify existing dispersant effectiveness tests that have been completed on Alaskan oils under conditions similar to those that exist in these two regions and identify gaps in the knowledge of dispersant effectiveness (see Section 5 of this report);
6. Conduct dispersant effectiveness tests at medium scale to address the knowledge gaps (see Section 6 of this report);
7. Write a technical report on the study and a technical paper for presentation at a suitable oil spill conference or technical seminar (delivered under separate cover).

3 Background

In the event of an offshore oil spill rapid decisions must be made with regard to the best course of action to mitigate potential effects of the spillage. Chemical dispersants are one of the tools to be considered. The initial question to be answered when deciding if dispersant application is an appropriate action is "Will the dispersant be effective in removing a significant percentage of the oil from the surface?" If not, then the dispersant operation would not be considered. If chemical dispersants are deemed to be potentially effective other issues such as a) the logistical feasibility of getting the dispersant to the spill site; b) applying it at the appropriate dosage; and c) the net environmental benefit of using the dispersant must also be considered in the decision making

process prior to the final approval for dispersant use. This report addresses only the issue of dispersant effectiveness.

The potential effectiveness of a chemical dispersant will depend on the type of dispersant used, the type and weathered state of the oil to be treated, and the prevailing environmental conditions at the time of application (water temperature, water salinity, wave energy present and presence of ice). A number of dispersant effectiveness studies have been completed using Alaskan oils, in warm and cold waters, in different water salinities, and in the presence of ice, including several studies funded by the US Department of the Interior. This report provides a focused review of this research, a review of the range of environmental conditions that could be encountered in the two regions during a dispersant application operation and the identification of additional research requirements regarding the use of dispersants specific to the U.S. Beaufort and Chukchi Sea regions. Meso-scale tank tests of dispersant effectiveness on four Alaskan crude oils have also been conducted in this study to help fill in some of the knowledge gaps on dispersant use under conditions that could be encountered in these regions.

4 Typical Environmental Conditions in the U.S. Beaufort and Chukchi Seas that Affect Dispersant Effectiveness

The primary environmental factors that have been shown to influence dispersant effectiveness include: wave energy present at the time of dispersant application or shortly after the application; water salinity; water temperature (primarily the effect of temperature on the oil's properties of viscosity and pour point); and presence and concentration of ice (and the influence of the ice on the surface and sub-surface mixing energy). The range of conditions that exist for these four parameters in the U.S. Beaufort and Chukchi Sea regions are documented along with their variability on both a seasonal and spatial basis on a scale appropriate for decision purposes.

4.1 Water Salinity

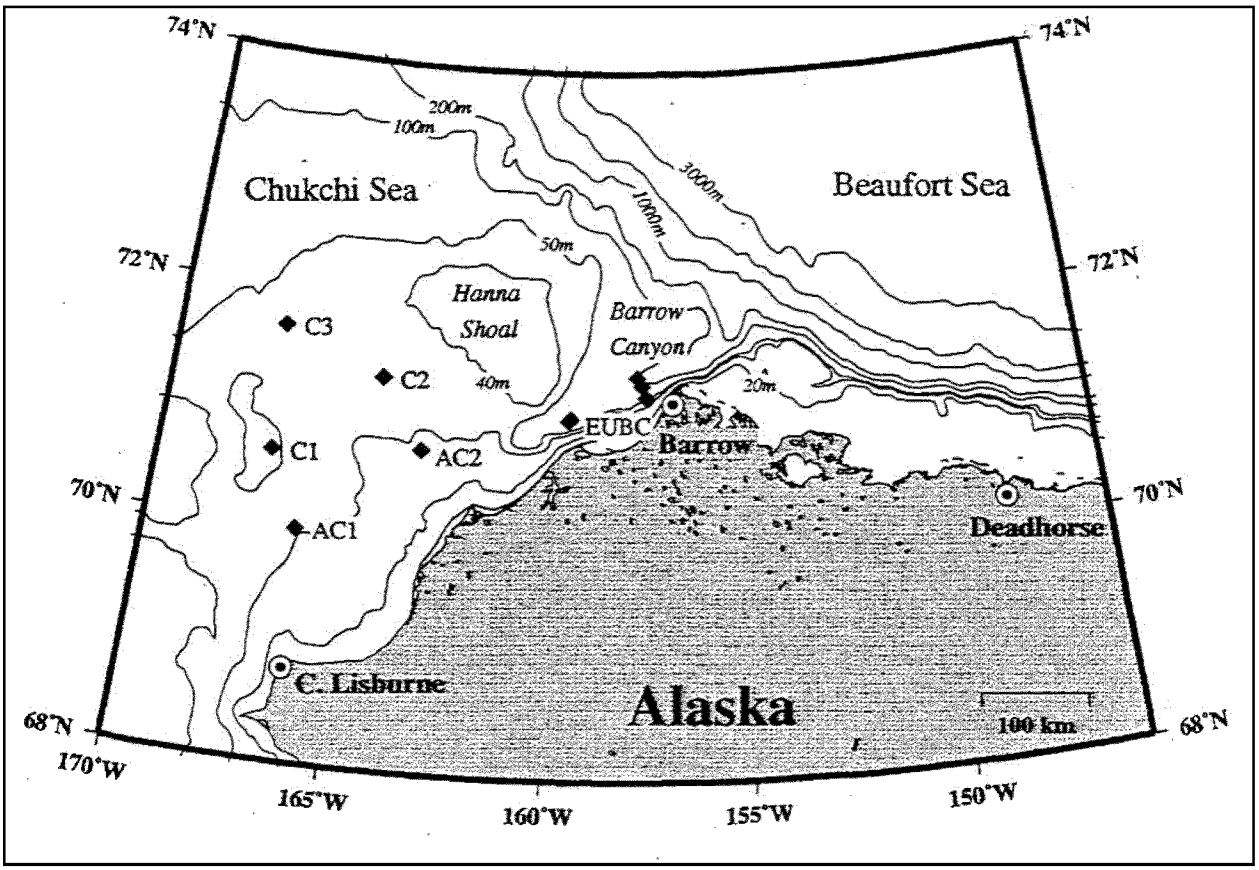
With the exception of isolated near shore fresh water outlets there is minimal variation, both temporally and spatially, in surface water salinity throughout the U.S. Chukchi and Beaufort Sea regions, at least from a chemical dispersant effectiveness standpoint. The performance of most chemical dispersants is generally not affected by salinity in the range of 25 to 35 ppt (SL Ross

2010). Studies at specific offshore sites have identified surface water salinity variation between 28 and 34 ppt (Weingartner and Danielson 2010, Weingartner et al. 2005). Weingartner (1998) also measured surface water salinity at various locations in the Chukchi Basin (see Figure 4-1). Seasonal surface water salinities were shown to vary between about 30 to 34 ppt (Figure 4-2), well within the range for effective chemical dispersant use. Figure 4-3 shows salinity measurements, also made by Weingartner, along an east-west transect from Barrow AK to Wrangel Island in the west. Measured salinities in all of these cases ranged from about 29 to 32 ppt.

Measured surface water salinity in the Beaufort Sea offshore region ranges between 27 and 34 ppt (Aagaard et al,1988, Proshutinsky et al, 2003, Weingartner et al. 2006). Figure 4-7 and Figure 4-8 show salinity profiles measured by Aagaard for the western and eastern extents of the Beaufort Sea (transects W and D shown in Figure 4-6). The salinities are somewhat lower 28 to 29 ppt in the east versus 28 to 31 in the west. Weingartner's salinity measurements were made at the sites along the outer shelf identified in Figure 4-4. Figure 4-5 shows the measured surface water salinities that were taken along the shelf. The salinities vary from about 32 ppt in the west to about 29 in the east. The salinities in all reported cases for the offshore Beaufort Sea region are sufficiently high that chemical dispersant effectiveness would not be significantly affected. Proshutinsky also concluded that "In ice-free regions, seasonal temperature fluctuations reach up to several degrees, whereas salinity fluctuations are small."

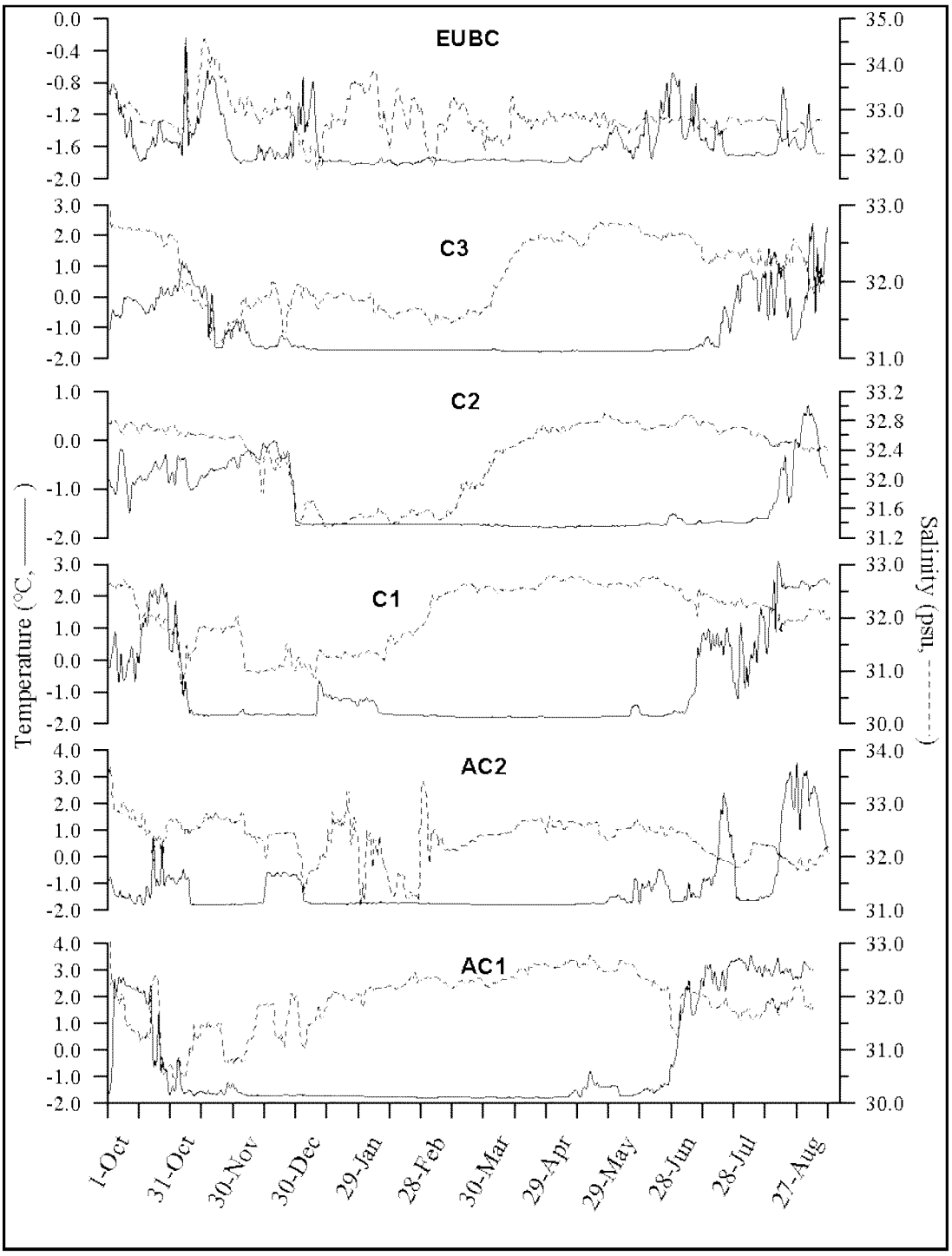
Water salinities in the nearshore area of the Beaufort Sea can be considerably lower than the offshore areas for short periods of the year due to the influence of fresh water river outflows and ice melt. Fresh water from river outflow can form a 1 to 2 m deep lens under the landfast ice that may extend up to 25 km offshore from the major river mouths (Weingartner et al. 2005). The surface water salinities in these areas approach that of fresh water during the early ice breakup period and prior to the mixing of the upper and lower water layers by strong winds and waves. The presence of this near shore fresh water during this period could hinder the effectiveness of chemical dispersants. However, dispersants are generally not approved for use in waters less than 10 m, so this may not be an issue depending on the extent of the surface freshwater plume offshore.

Nearshore, bottom, salinity measurements in about 10 m water depths offshore from the Sagavanirktok River (see Figure 4-9 for mooring locations) reveal bottom water salinities as low as 14 ppt early in the spring melt and freshet period (Weingartner et al. 2005). During breakup the bottom water salinity drops from greater than 30 ppt over a period of about 1 week at the beginning of August to as low as 15 ppt and then climbs back up to 30 by the end of August as the surface lens of fresh water is mixed down into the water layer. Figure 4-10 shows the measured bottom water salinity in about 7 m of water at the Dinkum mooring. These measurements confirm the presence of the surface fresh water lens and its eventual influence on water salinity at depth.



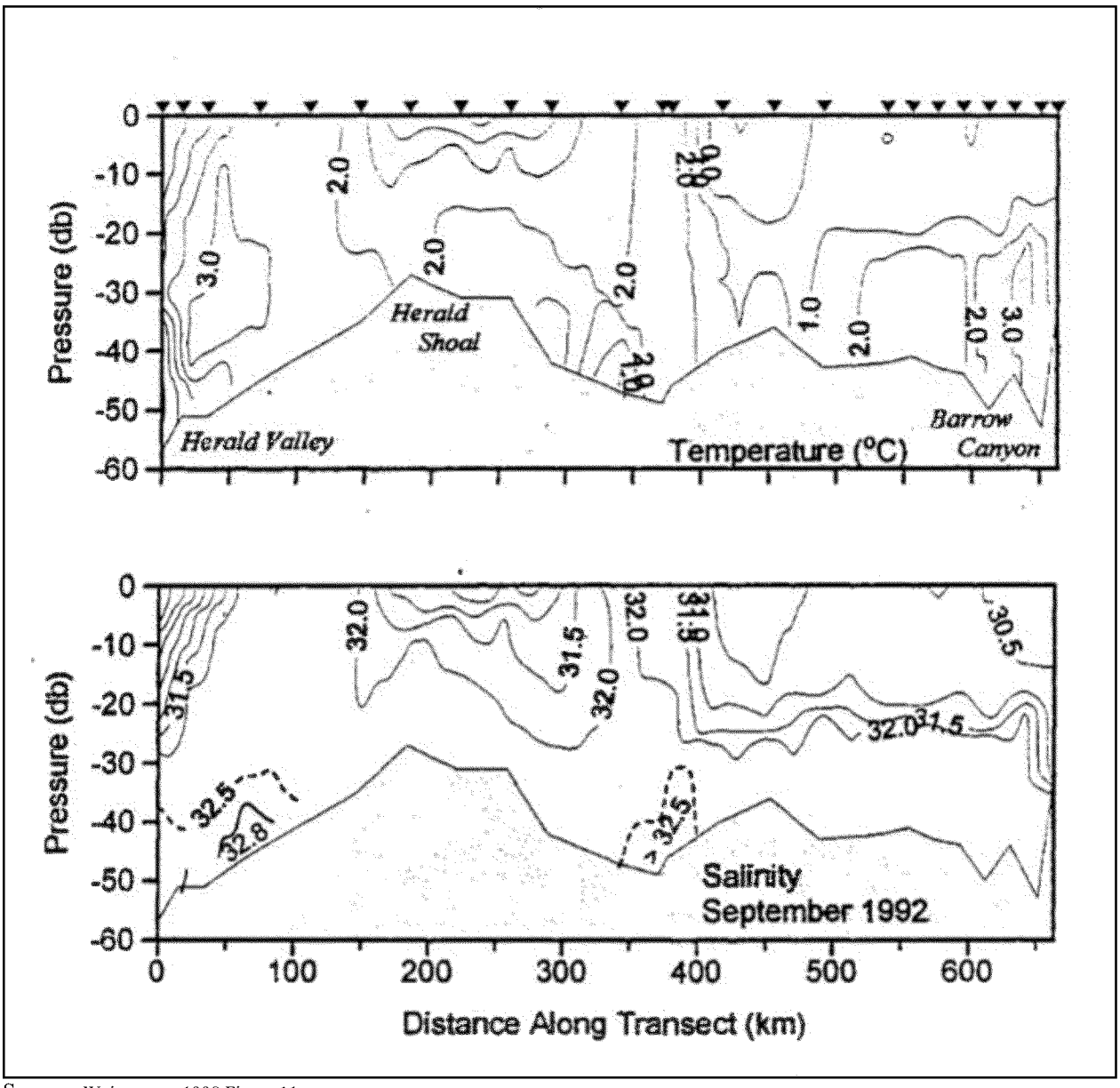
Source: Weingartner 1998 Figure 2

Figure 4-1 Location of Temperature and Salinity Measurements Reported in Figure 1-2



Source: Weingartner 1998 Figure 8

Figure 4-2 Seasonal Temperature and Salinity Variation on the Chukchi Shelf



Source: Weingartner 1998 Figure 11

Figure 4-3 Salinities and Temperatures Along an E-W Transect in the Chukchi Sea (Wrangel Is to Barrow)

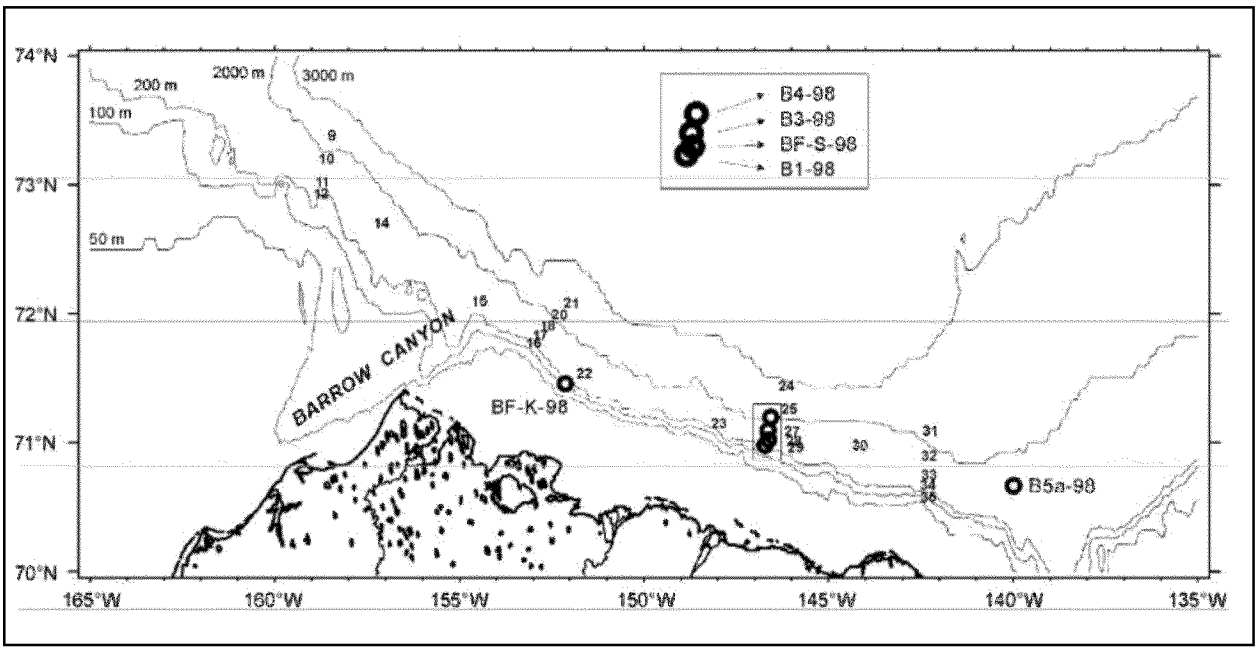


Figure 4-4 Mooring and Hydrographic Station Locations (source: Weingartner 2006 Figure 7)

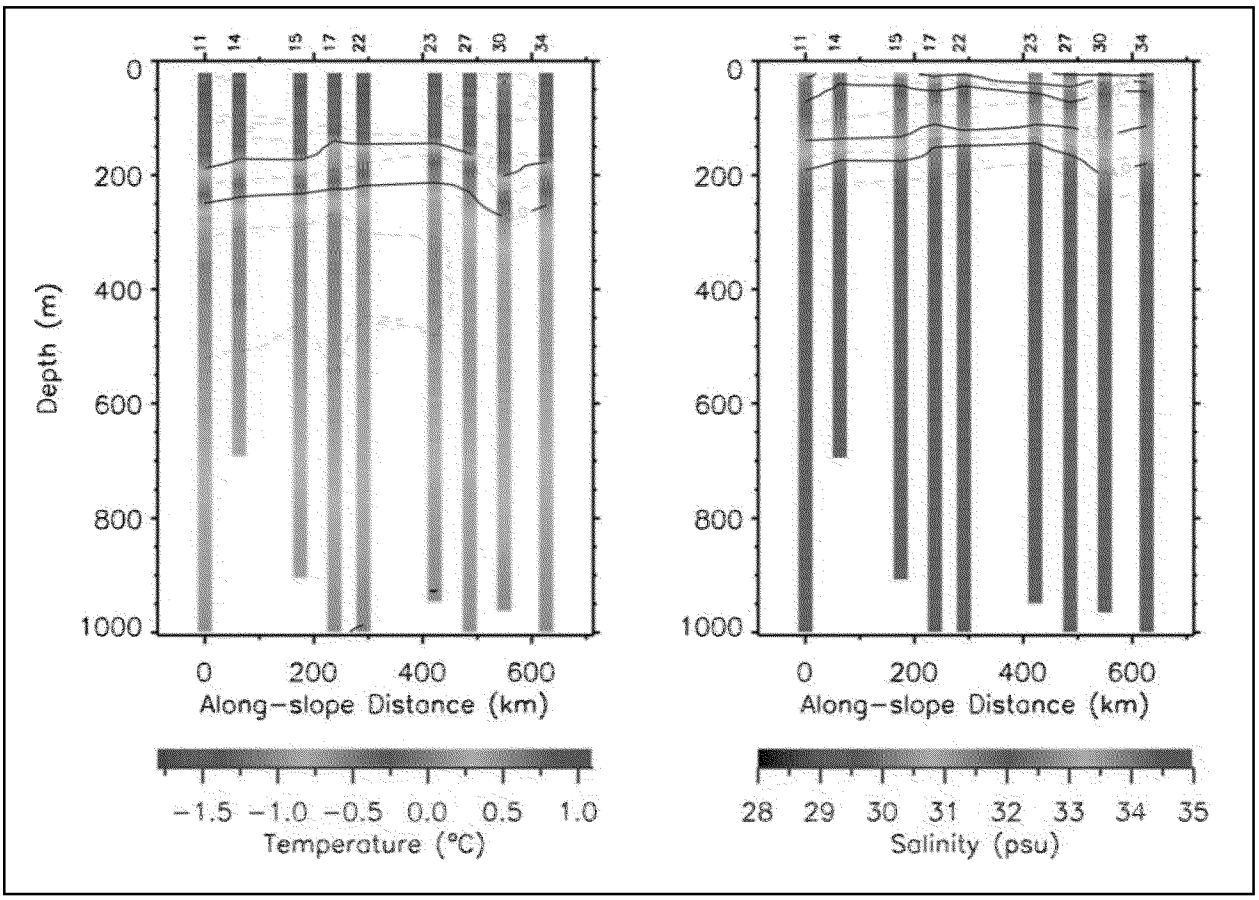


Figure 4-5 Salinity and Temperature Measurements Along Alaskan BS Slope (source: Weingartner 2006 Figure 36)

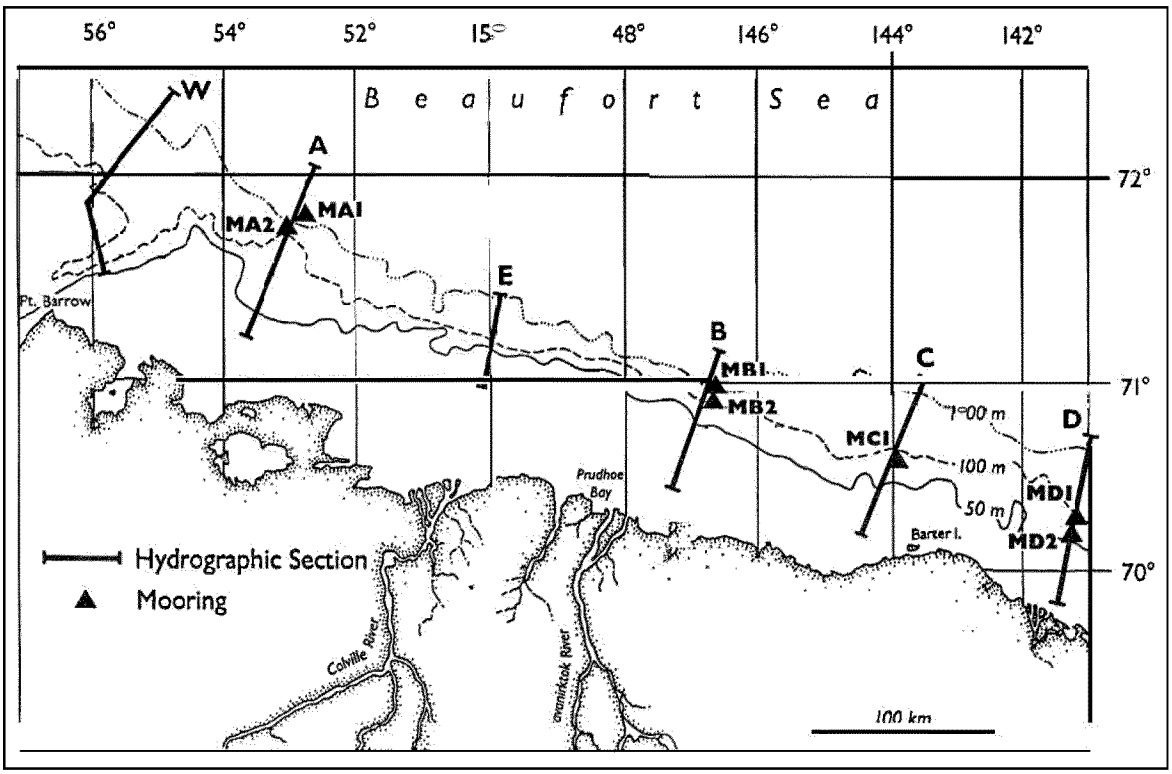


Figure 4-6 October Measurement Transects and Mooring Locations (source: Aagaard 1988 Figure 1)

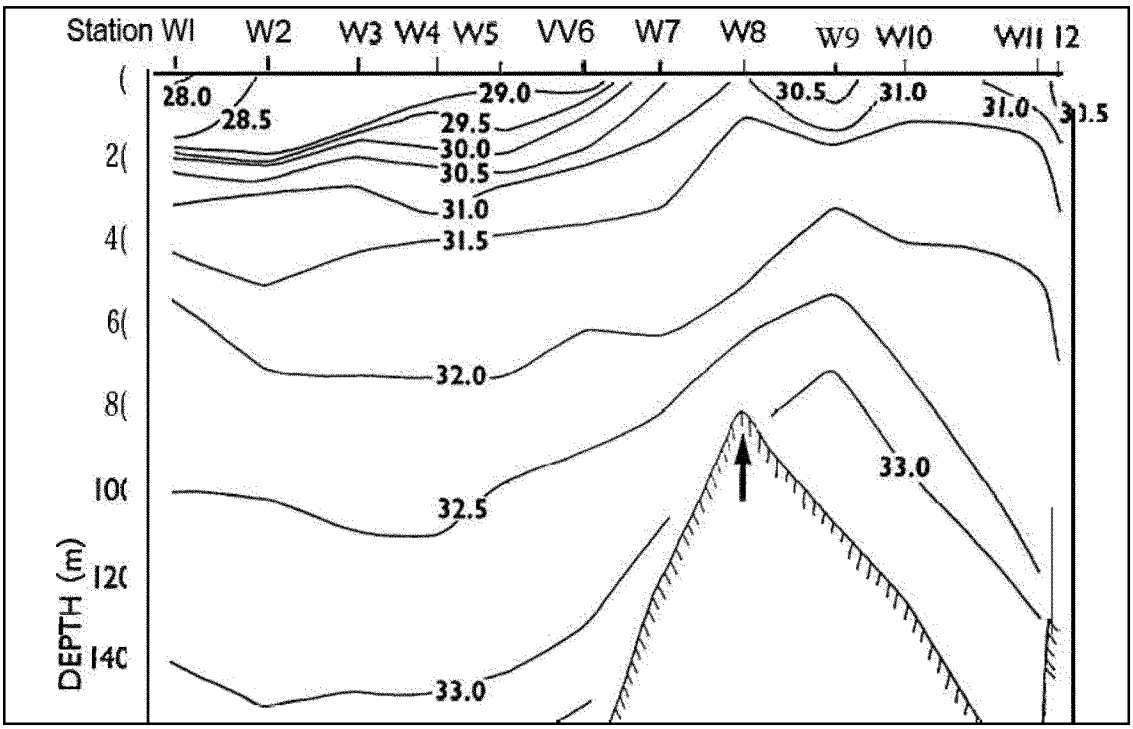


Figure 4-7 October 1988 Water Salinities at Transect W (source: Aagaard 1988 Figure 8)

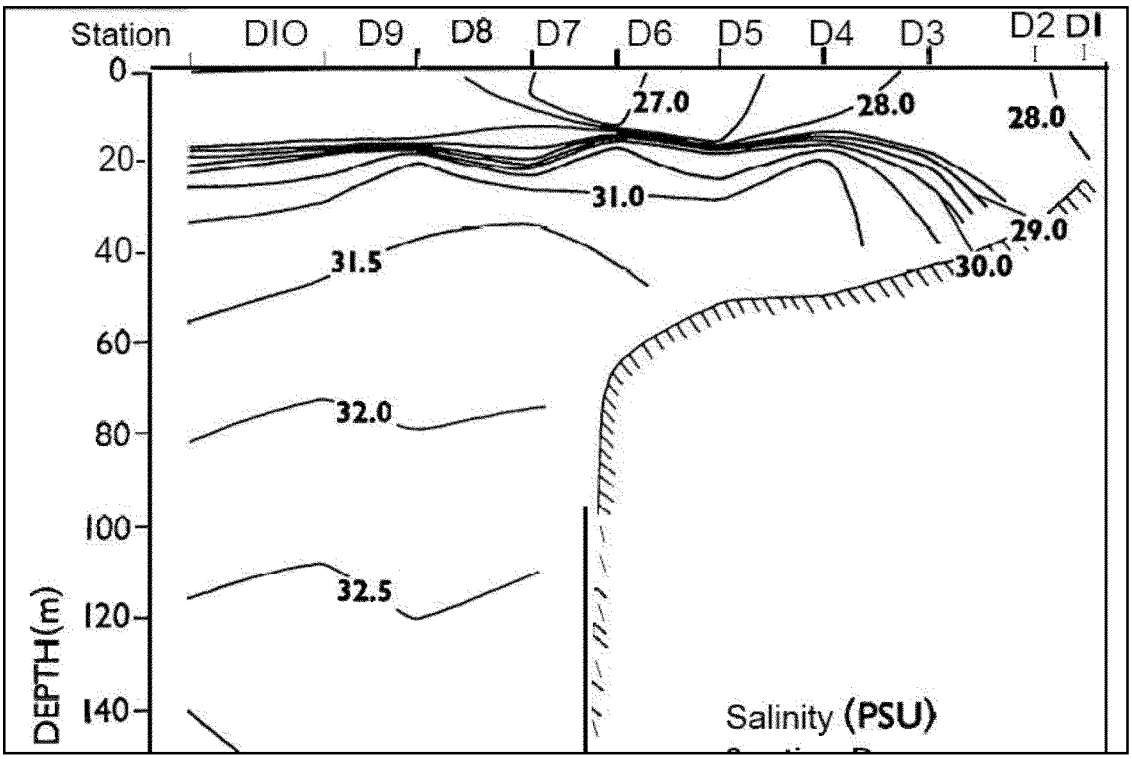


Figure 4-8 October 1988 Water Salinities at Transect D (source: Aagaard 1988 Figure 53)

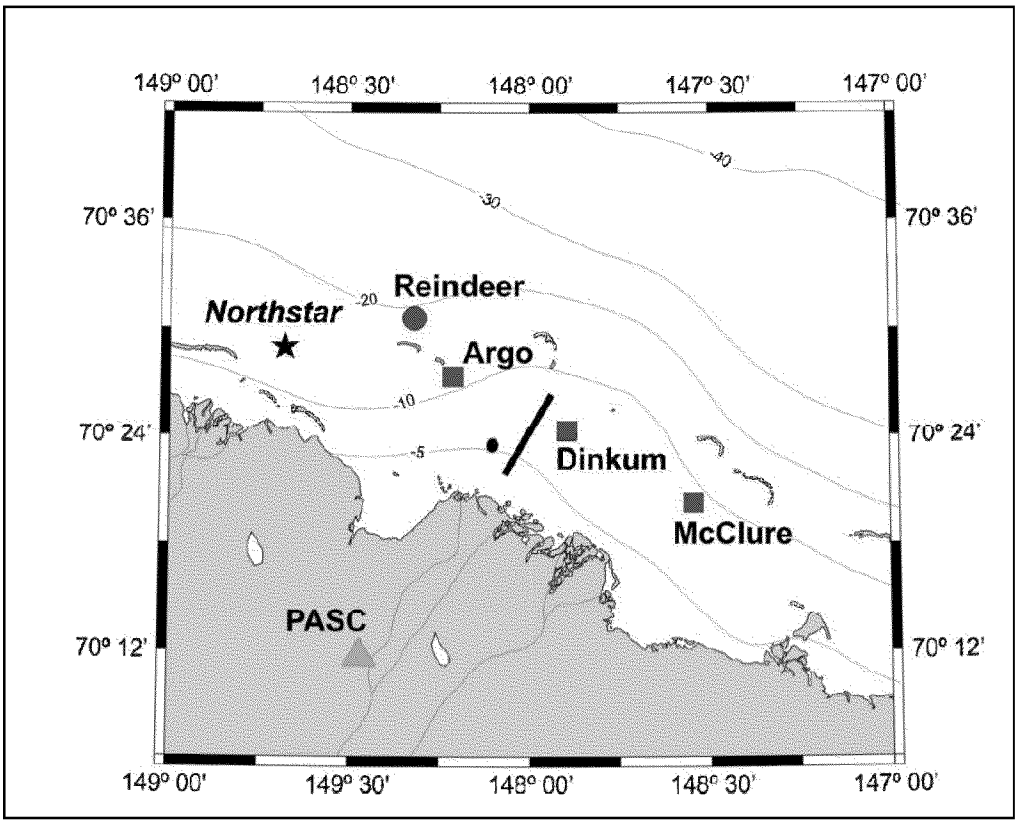


Figure 4-9 Nearshore Instrument Locations (source Weingartner et al. 2005)

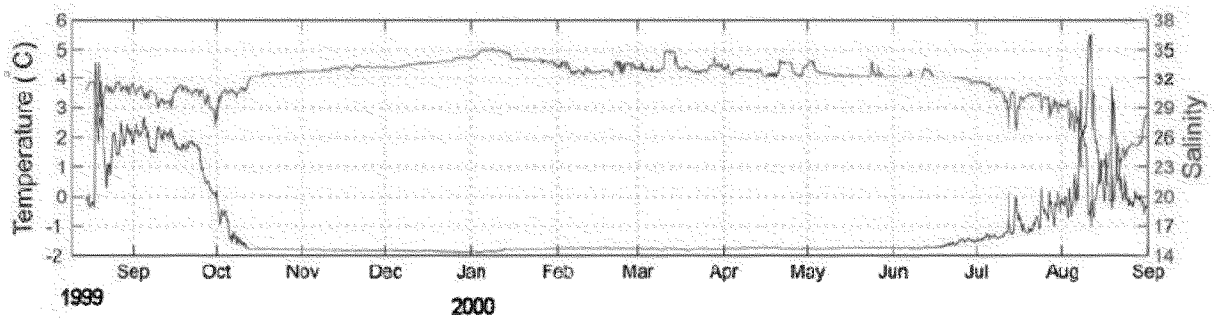


Figure 4-10 Nearshore Water Salinity in Beaufort Sea at Dinkum Deployment (source: Figure 45 Weingartner et al. 2005)

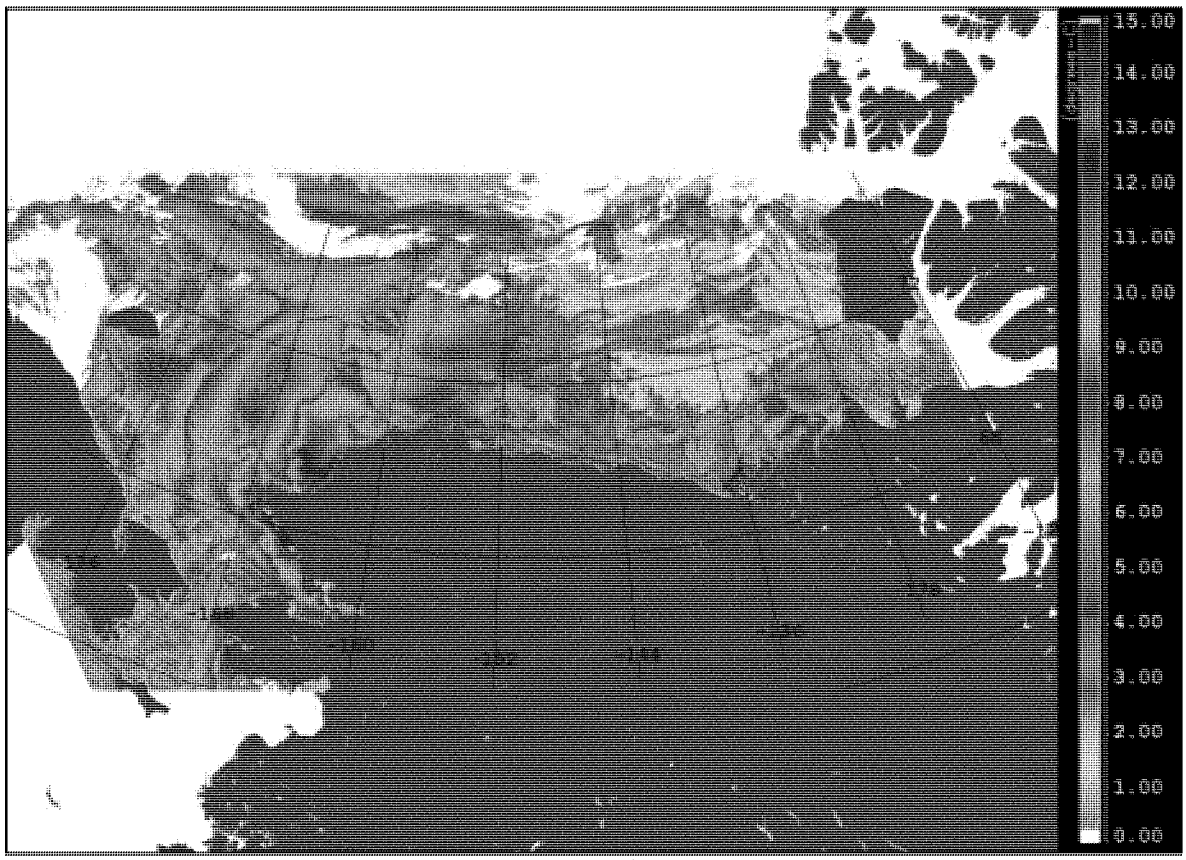
4.2 Water Temperature

The dispersibility of a crude oil is a strong function of its viscosity, which in turn is often very temperature dependent. As crude oils cool their viscosities increase and with increasing viscosities there is a potential for the reduction of dispersant effectiveness. If the water temperature is below the pour point of the oil (and the oil's temperature has reached the water temperature) the oil may not be fluid and is very viscous. Under these conditions the dispersant does not easily mix with the oil when applied. As a result of the combination of the poor mixing of the dispersant into the oil and the high viscosity of the oil dispersants are not effective at these temperatures. The chemical dispersibility of the crude oil is affected by the temperature only as it affects the viscosity of the oil. The oil's viscosity is affected by the water temperature on which it sits and during sunny days by the heating of the surface of the oil by the sun. Different crude oils can have very different viscosities at the same temperature and many can be quite fluid at temperatures near freezing. There is really no water temperature that will completely restrict the use of chemical dispersant. The oil viscosity – temperature relationship must be considered for each candidate oil before an evaluation of the potential for dispersant effectiveness can be made.

The surface water temperatures in the Chukchi and Beaufort Seas in the open water seasons can vary from close to freezing (-2 °C) to upwards of 10 °C. Figure 4-2, Figure 4-3, Figure 4-5, and Figure 4-10 all show surface water temperatures in the Chukchi and Beaufort Seas that fall with this range. The satellite image in Figure 4-11 shows August surface water temperatures in the US Beaufort Sea ranging from 2 to 9 °C and in the Chukchi Sea from 4 to 14 °C with considerable

spatial variability in both regions. The wide spatial variation in surface water temperatures in both the Chukchi and Beaufort Seas can be seen in the extensive imagery catalogued at http://mather.sfos.uaf.edu/~mschmidt/ims_summary_new.html.

The decision to use dispersants from a potential effectiveness standpoint in these regions will require a case-by-case evaluation of the prevailing water temperature and the oil viscosity-temperature relationship.



Source: http://mather.sfos.uaf.edu/~mschmidt/ak_beaufort_sea_2007/ims_beaufort_aug_2007.html.

Figure 4-11 August 22, 2007 MODIS sea surface temperature image of the Chukchi Sea and Beaufort Sea

4.3 Ice Cover

The presence of greater than 9/10ths ice cover eliminates the possibility of using conventional surface applied dispersant operations. The presence of the ice either encapsulates the oil making it impossible to target with aerial applied dispersant or dampens the surface energy such that there is insufficient energy to break the oil into droplets once treated. In ice conditions with less

than 3/10ths cover chemical dispersants will perform much the same as in open water conditions since the surface mixing energy is not overly dampened by the presence of the ice. The performance of dispersants in 3/10ths to 8/10ths ice cover without additional mixing energy applied is somewhat uncertain. Research suggests that performance may be enhanced in these conditions by the energy generated at the ice edge as the ice pieces jostle even under low wave energy (SL Ross 2002, 2006a). Additional research on the potential for dispersant use under partial ice cover conditions is currently being considered (OGP 2014). Regardless, it is instructive to identify the potential periods of open water when traditional surface dispersant application operations could be successful. In the Chukchi Sea region open water periods can exist in the months from June through November depending on the year based on an assessment of the US National Snow and Ice Data Center's archived ice cover data located at the following URL: (http://nsidc.org/data/seaice_index/archives/image_select.html). Open water is most common in the months of July through October in this region but the shoulder months of June and November may present dispersant application opportunities depending on the ice year. In the Beaufort Sea region the maximum likely extent for open water dispersant use is from July to October with the more likely season being from August to October. Table 4-1 shows the months when the two regions were primarily in open water or low ice concentration conditions for the years from 1998 to 2013.

Table 4-1 Open Water period in US Chukchi and Beaufort Sea Regions

Year	Chukchi Sea Open Water Months	Beaufort Sea Open Water Months
1998	July, Aug., Sept., Oct., Nov	~~July~~, Aug., Sept., Oct.
1999	July, Aug., Sept., Oct.	Aug., Sept., ~~Oct.~~
2000	July, Aug., Sept., Oct., ~~Nov~~[1]	Aug., Sept., Oct.
2001	July, Aug., Sept., Oct.	~~Aug.~~, Sept.
2002	~~June~~, July, Aug., Sept., Oct., Nov	Aug., Sept., Oct.
2003	June, July, Aug., Sept., Oct., Nov	Aug., Sept., Oct.
2004	July, Aug., Sept., Oct., ~~Nov~~	Aug., Sept., Oct.
2005	~~June~~, July, Aug., Sept., Oct., ~~Nov~~	Aug., Sept., Oct.
2006	July, Aug., Sept., Oct., Nov	Aug., Sept., Oct.
2007	~~June~~, July, Aug., Sept., Oct., ~~Nov~~	Aug., Sept., Oct.
2008	July, Aug., Sept., Oct.	~~July~~, Aug., Sept., Oct.
2009	July, Aug., Sept., Oct.	July, Aug., Sept., Oct.
2010	July, Aug., Sept., Oct., ~~Nov~~	Aug., Sept., Oct.
2011	~~June~~, July, Aug., Sept., Oct.	Aug., Sept., Oct.
2012	July, Aug., Sept., Oct.	Aug., Sept., Oct.
2013	July, Aug., Sept., Oct.	Aug., Sept., Oct.
[1]Crossed out months had partial open water in the region		
Source: imagery at http://nsidc.org/data/seaice_index/archives/image_select.html		

An additional source of information on ice cover for the central Chukchi Sea area is Figure 4-12. This shows the open water and ice cover conditions for the Burger drilling prospect from 1995 to 2011. The results are similar to the general trends identified in Table 4-1.

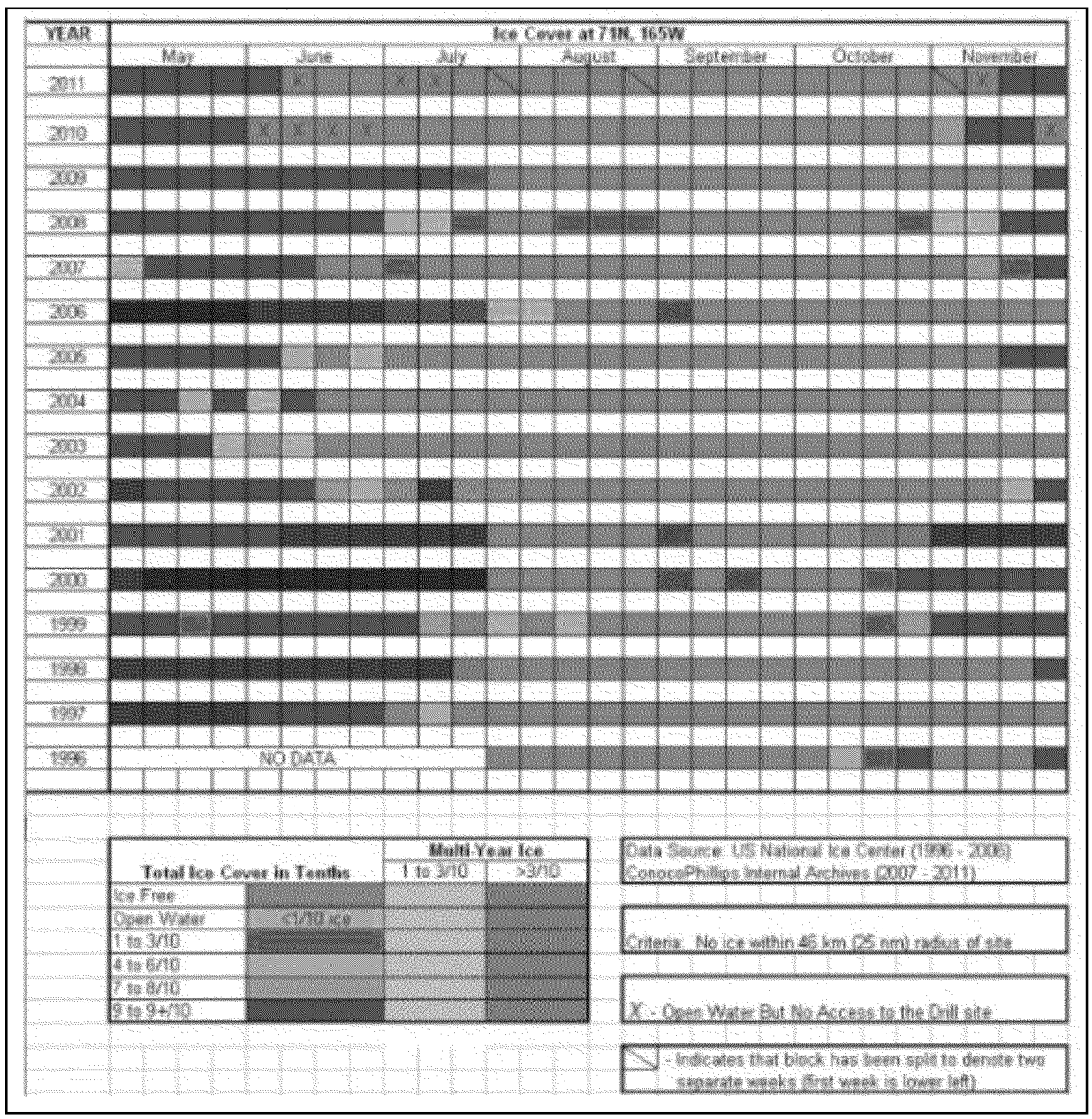
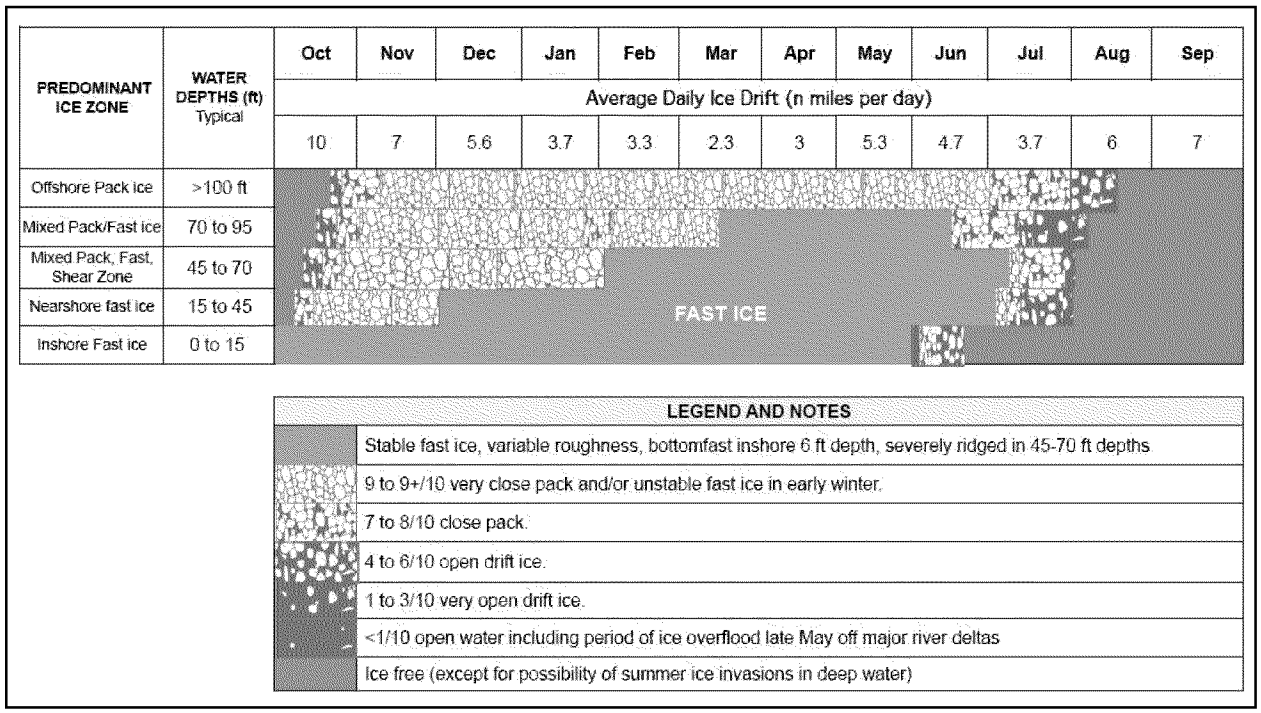


Figure 4-12 Ice Cover at Burger prospect in Central Chukchi Sea (source: Wang et al. 2012)

An additional source of information on ice cover for the US Beaufort Sea north of Point Thompson around Shell's Sivulliq drilling prospect is Figure 4-13. This shows the typical open water and ice cover conditions for the Shell's Sivulliq drilling prospect. The results are similar to the general ice cover trends for the Beaufort Sea Region identified in Table 4-1.



PREDOMINANT ICE ZONE	WATER DEPTHS (ft) Typical	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
		Average Daily Ice Drift (n miles per day)											
		10	7	5.6	3.7	3.3	2.3	3	5.3	4.7	3.7	6	7
Offshore Pack ice	>100 ft												
Mixed Pack/Fast ice	70 to 95												
Mixed Pack, Fast, Shear Zone	45 to 70												
Nearshore fast ice	15 to 45												
Inshore Fast ice	0 to 15												

LEGEND AND NOTES
Stable fast ice, variable roughness, bottomfast inshore 6 ft depth, severely ridged in 45-70 ft depths
9 to 9+/10 very close pack and/or unstable fast ice in early winter.
7 to 8/10 close pack.
4 to 6/10 open drift ice.
1 to 3/10 very open drift ice.
<1/10 open water including period of ice overflood late May off major river deltas
Ice free (except for possibility of summer ice invasions in deep water)

Figure 4-13 Ice Cover at Sivulliq prospect north of Point Thompson in the Beaufort Sea (source: Dickins 2007)

In periods of complete ice cover dispersants could be used in conjunction with ice-breaker support and the application of additional mixing energy through the azimuthal stern drive propeller systems deployed by modern icebreakers (SL Ross 2005, 2006a, 2006c). Subsea dispersant injection during a subsurface well blowout is another type of dispersant operation that could be conducted in a complete ice cover environment. Dispersant effectiveness and net environmental benefit considerations would have to be evaluated on a case- by-case basis before implementing these types of operations.

4.4 Wave Energy

Long term historical wave height data is not available in the U.S. Chukchi and Beaufort Sea regions. A few recent years of wave data at specific locations are available from summer buoy deployments (see http://www.aoos.org/aoos-data-resources) but this data is insufficient both temporally and spatially to quantitatively assess the potential for dispersant effectiveness in the region. Long term wind data are, however, available for the region through shore-based weather stations and offshore hindcast analyses. Wave heights can be derived from wind speed data

through the Beaufort wind scale in the absence of actual measured wave height data and that approach has been taken to estimate wave heights for this project. The Beaufort scale is provided in Table 4-2. The wave height and wind speed data from this table have been plotted in Figure 4-14 to develop a polynomial prediction of wave height as a function of wind speed.

Table 4-2 Beaufort Wind Scale

Force	Wind (Knots)	WMO Classification	Appearance of Wind Effects	
			On the Water	On Land
0	Less than 1	Calm	Sea surface smooth and mirror-like	Calm, smoke rises vertically
1	1-3	Light Air	Scaly ripples, no foam crests	Smoke drift indicates wind direction, still wind vanes
2	4-6	Light Breeze	Small wavelets, crests glassy, no breaking	Wind felt on face, leaves rustle, vanes begin to move
3	7-10	Gentle Breeze	Large wavelets, crests begin to break, scattered whitecaps	Leaves and small twigs constantly moving, light flags extended
4	11-16	Moderate Breeze	Small waves 1-4 ft. becoming longer, numerous whitecaps	Dust, leaves, and loose paper lifted, small tree branches move
5	17-21	Fresh Breeze	Moderate waves 4-8 ft taking longer form, many whitecaps, some spray	Small trees in leaf begin to sway
6	22-27	Strong Breeze	Larger waves 8-13 ft, whitecaps common, more spray	Larger tree branches moving, whistling in wires
7	28-33	Near Gale	Sea heaps up, waves 13-19 ft, white foam streaks off breakers	Whole trees moving, resistance felt walking against wind
8	34-40	Gale	Moderately high (18-25 ft) waves of greater length, edges of crests begin to break into spindrift, foam blown in streaks	Twigs breaking off trees, generally impedes progress
9	41-47	StrongGale	High waves (23-32 ft), sea begins to roll, dense streaks of foam, spray may reduce visibility	Slight structural damage occurs, slate blows off roofs
10	48-55	Storm	Very high waves (29-41 ft) with overhanging crests, sea white with densely blown foam, heavy rolling, lowered visibility	Seldom experienced on land, trees broken or uprooted, "considerable structural damage"
11	56-63	Violent Storm	Exceptionally high (37-52 ft) waves, foam patches cover sea, visibility more reduced	
12	64+	Hurricane	Air filled with foam, waves over 45 ft, sea completely white with driving spray, visibility greatly reduced	

Source: http://www.spc.noaa.gov/faq/tornado/beaufort.html

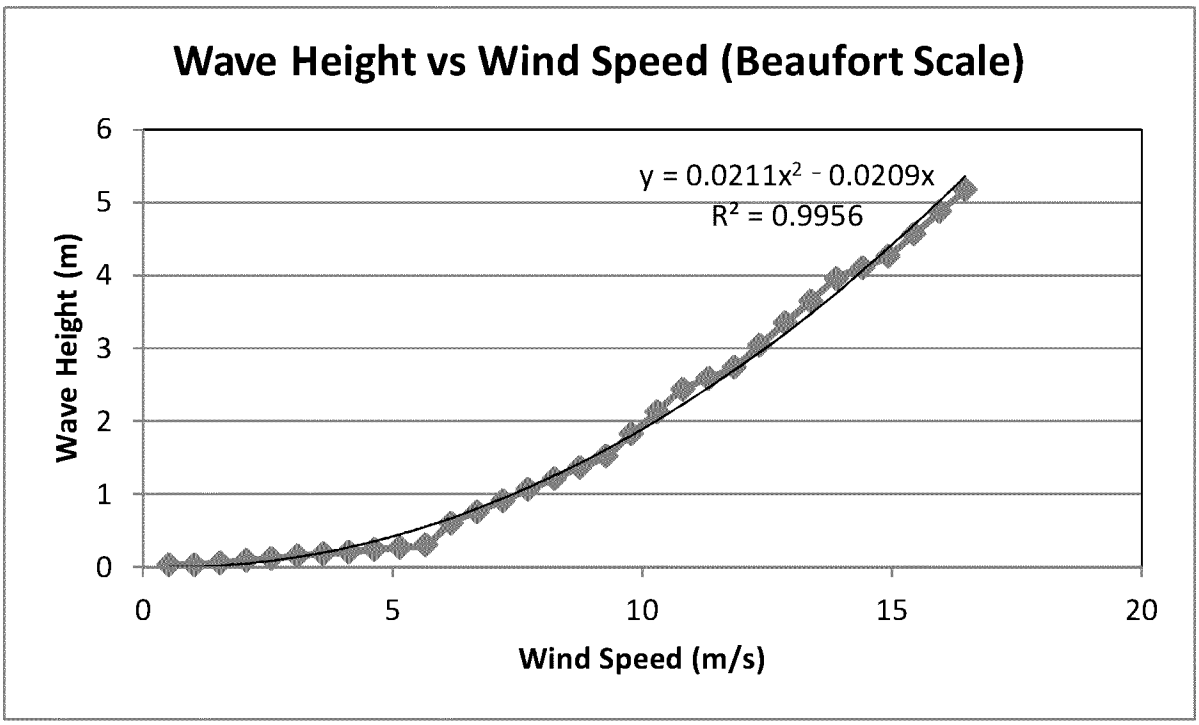


Figure 4-14 Beaufort Wind Scale Wave height Wind Speed Correlation

Land based weather station data were acquired from NOAA for a number of locations along the Chukchi and Beaufort coast lines and these data sets were evaluated for use in the project. Unfortunately, the weather station data had significant data gaps over the past 10 years of data and was not of sufficient quality for use in this project. Fortunately, the Bureau of Ocean Energy Management (BOEM) funded a project to develop a hindcast wind data set for the U.S. Chukchi and Beaufort Sea regions that spans the 31 year period from 1979 to 2009. The data set is known as CBHAR (Chukchi/Beaufort High-resolution Atmosphere Reanalysis). Hourly, ten meter data from five grid points from the BOEM data set have been acquired for this project for use in estimating wave heights in the region. Locations of the offshore grid points selected for analysis are provided in Table 4-3. These locations are mapped in Figure 4-15.

Table 4-3 BOEM Hindcast Wind Data Grid Point Locations

Station Identifier	Longitude	Latitude	Nearby Land Weather Station
Station1	-167.5	69.0	Cape Lisbourne
Station2	-166.0	71.0	Wainwright
Station3	-156.0	72.0	Barrow
Station4	-148.0	71.0	Prudhoe Bay
Station 5	-140.0	70.0	Barter island

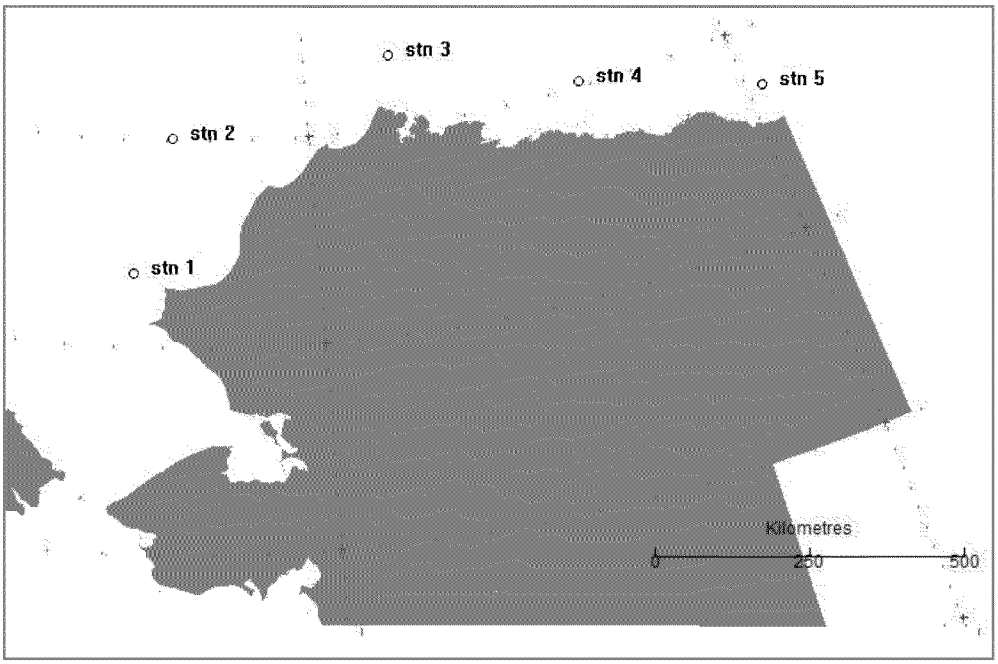


Figure 4-15 Hindcast Wind Grid Point Locations

The Beaufort wind-wave height correlation from Figure 4-14 has been applied to the BOEM hindcast wind data to provide wave height estimates for use in dispersant effectiveness evaluation across the region. The criteria in Table 4-4 have been used to define the times when aerial chemical dispersant application by large aircraft would be possible based on prevailing wind speeds and likely effective based on wave conditions and ice cover. These criteria were established for use in a dispersant use GAP analysis (SL Ross 2011). The rationale for the selection of these criteria is as follows.

Dispersants can be applied by large aircraft until wind speeds are high enough to impair the dispersant spraying operation. At speeds greater than 15 m/s large aircraft have difficulty maintaining their spray path and the high winds affect the dispersant fallout (Exxon 2000). Dispersants are most effective when slicks of fresh or lightly weathered oils can be sprayed with an adequate dose of effective dispersant product in the presence of breaking waves. In offshore environments breaking waves develop when wind speeds exceed 3.5 to 5.4 m/s and waves are 0.5 to 1 m in height. Dispersants can be applied in non-breaking wave conditions, where dispersion might not occur immediately, if breaking waves are likely to occur within a

reasonable time after dispersant application. Research has shown that dispersants applied to slicks on calm seas will cause effective dispersion if the treated slicks are exposed to breaking waves within 48 hours (Lewis, et al. 2010). Dispersant effectiveness begins to be impaired at wave heights of 3 m and above, as at this point waves begin to entrain a considerable proportion of the slick into the water and hold it in suspension temporarily, making it difficult to hit the oil with dispersant spray.

Table 4-4 Operating Limits for Large Aircraft Dispersant Operations

Aerial Dispersant Application (large aircraft)	Favorable	Marginal	Not Possible
Wind Speed (m/s)	<13	>=13 to <=15	>15
Wave Height (m)	>0.6 and <3.0 OR >0.0 and <3.0 if >=0.6 in following 48 h	>=3.0 and <=4.6	> 4.6 OR <0.6 if <0.6 in following 48 h
Ice Cover (10^{ths})	<5/10	5/10 to 9/10	>9/10

The conditions identified in Table 4-4 were applied to the hourly hindcast wind data (and wave heights estimated using the correlation in Figure 4-14) over the full 31 years of data and for the past 10 years to determine the percentage of time that aerial dispersant applications could be effective. Table 4-5 summarizes the results of this assessment for wind station 1. The results for the assessment over the past 10 years (columns 5, 6 and 7) are very similar to the full 31 year analysis (columns 2, 3 and 4) with a maximum of a few percent difference in any given month. Based on this assessment chemical dispersant use would be favorable for 80 to 90% of the time at this location. This does not account for other operational limitations such as visibility and daylight hours as this was out of the scope of the study. Detailed tables for the remaining wind stations are provided in Appendix A.

Table 4-5 Percentage of Time Dispersants Would Be Effective at Wind Station 1 (Chukchi Sea Offshore Cape Lisbourne)

Percent of Time Dispersants Effective (48 hour Calm Wind Grace Period)						
	31 year Data Analysis (1979 to 2009)			10 year Data Analysis (2000 to 2009)		
Month	Favorable	Impaired	Not Favorable	Favorable	Impaired	Not Favorable
1	0	0	100 (ice covered)	0	0	100 (ice covered)
2	0	0	100 (ice covered)	0	0	100 (ice covered)
3	0	0	100 (ice covered)	0	0	100 (ice covered)
4	0	0	100 (ice covered)	0	0	100 (ice covered)
5	0	0	100 (ice covered)	0	0	100 (ice covered)
6	80	3	17	78	3	19
7	87	3	10	87	3	10
8	90	4	5	87	4	9
9	86	8	6	91	5	4
10	82	13	5	82	13	6
11	78	13	9	81	12	7
12	0	0	100 (ice covered)	0	0	100 (ice covered)

Table 4-6 shows the percentage of time that dispersants would be favorable for all 5 of the wind stations based on the most recent 10 years of data (column 5 from the detailed table results). For the months of July through October, where data exists for all wind stations, the least variability in the results occurs in September where favorable conditions across both regions range from 87 to 91%. The highest variability for these months is in July where favorable conditions range from 71 to 87%, with the Beaufort Sea region having the lowest percent of time with favorable conditions.

Table 4-6 Percentage of Time Dispersants Would Be Favorable Based on 10 Year Data Analysis: All Wind Stations

Month	Percent of Time Dispersant Effective (48 hr Calm Wind Grace Period)						
	10 Year Data Analysis (2000 to 2009): Favorable						
	stn 1	stn 2	stn 3	stn 4	stn 5	Average	Std. Dev.
1	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0
6	78	77	0	0	0	77	1
7	87	83	76	71	81	80	6
8	87	87	79	75	78	81	5
9	91	90	87	87	87	88	2
10	82	88	86	84	79	84	4
11	81	82	0	0	0	81	1
12	0	0	0	0	0	0	0

5 Historical Dispersant Effectiveness Testing on Alaskan Oils and Identification of Knowledge Gaps

This section summarizes the results of past chemical dispersant effectiveness studies that have been conducted on Alaskan oils for use in dispersant use decision-making. The extensive libraries of Environment Canada and SL Ross Environmental research Ltd., the Arctic and Marine Oil Spill Technical Seminar (AMOP), the International Oil Spill Conference Proceedings (IOSC), the Louisiana Universities Marine Consortium (LUMCON) library and other scientific Journals have been searched for this purpose.

5.1 Spill Related Properties of Alaskan Oils

The physical properties of a number of Alaskan production and pipeline oils are provided in Table 5-1 to show the range of oils that have been found in Alaska to date. A study of the change in the properties of the ANS blend that has been transported via the Alyeska pipeline over the past 30 years has also been recently conducted (SL Ross 2013). This study shows that the pipeline oil has progressively become less dense, less viscous and less likely to form stable emulsions. See Figure 5-1 and Figure 5-2. These property changes result in oil that is likely more amenable to chemical dispersion. The change in property is due to a change in the percentage of each production field's contribution to the total flow and possibly due to a change in the properties of the individual field oils themselves. Not enough data has been collected on the properties of the individual field crude oils to track their property changes over time. This information is provided to demonstrate that results from dispersant effectiveness tests conducted on a Prudhoe Bay pipeline crude in the 80's may not be comparable to effectiveness tests completed on Alaska North Slope crude in the 2000's due to different oil composition.

Table 5-1 Alaskan Oil Physical Properties

Oil Name	Density (g/cc) @ 15 °C			Viscosity (cP) @15 °C			Pour Point (°C)		
	fresh	2-day	2-week	fresh	2-day	2-week	fresh	2-day	2-week
ANS Blend (2004)[1]	0.870	0.920	0.930	10.2 (0%)	164 (30.8%)	374 (38.2%)	-21	3	9
ANS Blend (2012)	0.874	0.923	0.937	14 (0%)	156 (27%)	505 (35%)	<-18	-6	0
Endicott (2004)[1]	0.921	0.924	0.925	205 (0%)	247 (0.8 %)	342 (5.3%)	12	15	15
Kuparuk (2004)[1]	0.920	0.943	0.956	81 (0%)	351 (9.5%)	1391 (20.3 %)	<-21	<-21	-9
Lisbourne (1994)[2]	0.875	0.906	0.923	15.9 (0%)	187 (21.1%)	327 (30.6%)	-3	7	15
Northstar(2004)[1]	0.821	0.868	0.877	2.1 (0%)	14.4 (43.7%)	24.4 (52%)	<-21	0	3
Pt. McIntyre (1994)[2]	0.895	0.911	0.920	44 (0%)	125 (9.8%)	441 (18%)	-4	3	11

[1]OCS Study MMS 2008-033 Empirical Weathering Properties of Oil in Ice and Snow, Project Number 1435-01-04-RP-34501 (Mar Inc. 2008)
[2] Spill Related Properties of Fresh and weathered Alaskan Crude Oils (SL Ross 1994)

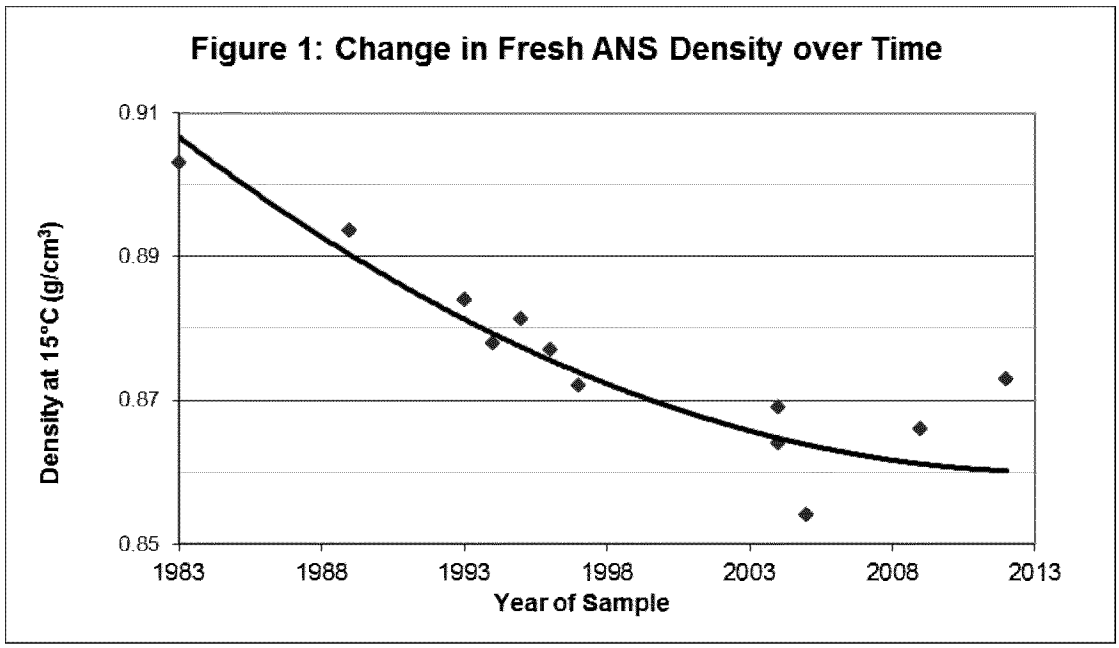


Figure 5-1 Change in Fresh ANS Density over Time

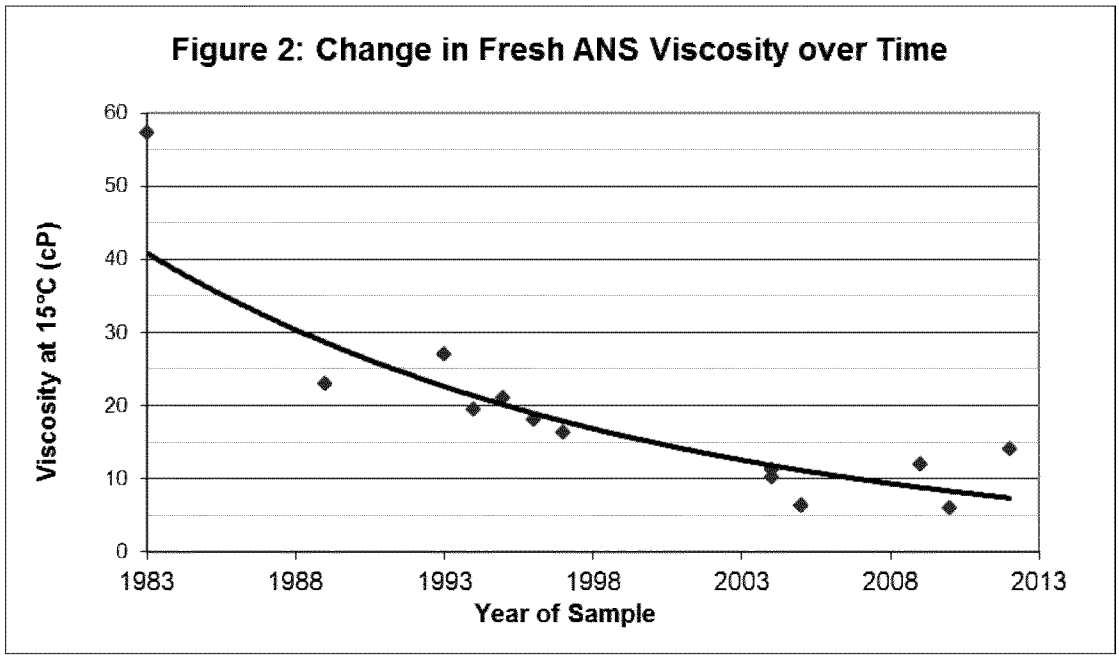


Figure 5-2 Change in Fresh ANS Viscosity over Time

5.2 Background - Mechanisms of Chemical Dispersion

When spilled on water, oil exhibits a cohesiveness or resistance to break up. This cohesive strength is due to the interfacial tension or contractile skin between the oil and water. A chemical dispersant sprayed onto an oil slick acts at the oil-water interface to reduce this interfacial tension. This action promotes the break-up of the oil film into droplets that disperse into the water phase. If the droplets are small enough they will have little buoyancy and will be carried away and diluted by normal ocean current and movement.

Surface active agents (surfactants) are the key components of a chemical dispersant. These compounds contain both a water compatible and an oil compatible group. Because of this molecular structure, the surfactant locates at the oil-water interface, reduces the interfacial tension, and thereby enables the oil slick to break up into finely dispersed oil droplets with the addition of significantly less energy than in the absence of the dispersant. Mackay and Hossain (1982) estimated that a concentration at an oil/water interface of 1 volume of dispersant per 500 volumes of oil will cause a 20-fold reduction in interfacial tension, say, from 20 dynes/cm to 1 dyne/cm. Since dispersants are normally applied at a ratio of 1 volume of dispersant to 20 volumes of oil, the implication is that only a few percent of the dispersant is being effective at any time, most being present in the bulk of the oil and thus remote from the interface.

Despite the great decrease in interfacial tension, some mixing energy is needed to promote movement and dispersion of the fine oil droplets into the water column. This energy can be supplied either by the natural motion and currents of the sea or by mechanical means such as work boats. The greater the available energy, the less dispersant or less effective dispersant is required.

A dispersant formulation also contains a solvent. Since many of the surface agents used in oil spill dispersant formulations are viscous, some form of solvent is necessary to reduce viscosity so that the mixture may be properly applied by conventional spray equipment. In addition, the solvent may act to depress the freezing point for low temperature usage and to enhance the mixing/penetration of the surfactant(s) into more viscous oils. In general, present day surfactants have demonstrated very low toxicity. In addition, these current formulations have substituted de-

aromatized hydrocarbons or aqueous solvents, resulting in very low toxicity dispersant formulations as compared with early formulations.

By their very nature, present-day dispersants include active ingredients that are more soluble in water than in oil. So the dispersant must be applied directly to the oil; otherwise the chemical will be lost to the water phase. Even when applied directly to the oil the chemicals will leach into the water, but the rate at which this happens is not well understood. Most products contain so-called "anionic" surfactants, like sulphosuccinates, in combination with "non-ionic" surfactants, like sorbitan ester surfactants (the SPANS® family of surfactants) and polyethoxylated sorbitan ester surfactants (the TWEEN® family). Studies on the subject (Knudsen et al. 1994, Hokstad et al. 1996) indicate that anionic surfactant compounds will rapidly leach into water, but that the rate of leaching of the non-ionic compounds is uncertain and dependent on a number of factors. Clearly, the leaching process is a complicated one, and it can be assumed that certain components of modern dispersant products will gradually leach from a layer of crude oil into the underlying water column and negatively affect the dispersibility of the oil. Tests conducted at Ohmsett demonstrated that under calm conditions enough dispersant remained with a treated oil slick to still be effective 2 to 6 days of exposure depending on the drift speed of the slick over the water surface and the exposure of the underside of the slick to surfactant free water (SL Ross 2007, 2008). This suggests that an oil spill can be dosed in relatively calm conditions with the expectation that the dispersant will remain with the oil and become effective when sea states and mixing energies increase after a few days.

5.3 Dispersant Effectiveness Test Results on Alaskan Oils

A review of scientific literature on the results of chemical dispersant effectiveness tests, specifically conducted on Alaskan crude oils, has been undertaken. Research that investigated chemical dispersant effectiveness under arctic conditions and in the presence of ice using other oil types has also been included in the review due to paucity of research in this area. Table 5-2 identifies the literature that has been reviewed and identifies the key variables that were studied in each test series. The review has focused on the parameters that could affect dispersant performance that are of specific concern to the arctic environment. These parameters include the test temperature, the water salinity, the mixing energy and the presence of ice. Oil type, dispersant type and dispersant dosage have also been considered in this review. With a few exceptions, only tests that have used Alaskan oil have been reviewed.

Only 10 of the 48 test programs reviewed studied dispersion in the presence of ice and only 7 of these varied the ice concentration in the test matrix and only two used Alaskan oil in the testing. Of the 48 studies reviewed, temperature was varied in 15, salinity was varied in 16, and mixing energy was varied in 29.

Most of the unique aspects of chemical dispersant use and effectiveness in the Arctic are due to the potential presence of ice in various forms and concentrations throughout the year. Mixing energy in the arctic environment may be reduced or eliminated due to the presence of ice. Melting ice may result in reduced surface water salinity. Ice may dampen overall surface water mixing or add localized mixing energy to the system. Water temperature is another important factor as cold water temperatures will reduce the dispersant and oil temperature, increase the oil viscosity and potentially reduce the effectiveness of dispersants due to the increased viscosity that may inhibit both the mixing of the dispersant into the oil and the breakup of the oil into small droplets. The impact on dispersant effectiveness of these factors is discussed in more detail in the following sections with specific reference to tests conducted on Alaskan crude oils.

5.4 Oil Type

At the present time the only oils being produced and transported (by pipeline to shore) in the Beaufort and Chukchi Seas are Northstar and Endicott crude oils and are the only crude oils that could be spilled directly into Alaskan offshore waters from present production fields. The Northstar oilfield is located six miles off the Beaufort Sea coast 11 miles northwest of Prudhoe Bay. Oil from this field is shipped to the Trans-Alaska Pipeline System via a trenched 10 inch pipeline to shore. The Endicott field is approximately four miles off the Beaufort Sea coast and 10 miles southeast of Prudhoe Bay. Oil from this field is shipped to the Trans-Alaska Pipeline System via a 16 inch pipeline to shore. No oils are presently being produced in Chukchi Sea waters.

Alaska North Slope Crude (ANS), or Prudhoe Bay crude as it was named in early test programs, has been the Alaskan oil of choice for most of the dispersant effectiveness tests conducted on Alaskan oils. This is evident in Table 5-2 where testing on Alaskan crudes other than the ANS blend crude occurred in only 5 of the research programs reviewed. The ANS or Prudhoe Bay crudes are both oils that were sampled from the Trans-Alaska Pipeline system that delivers Alaskan oil to Valdez. This oil is a blend of the oils produced from the various fields on the North Slope. Because this oil moves to the south by pipeline it is not likely to be spilled in the Beaufort or Chukchi Seas. As shown in Section 1 the physical properties of this Alaskan pipeline blend also have changed over the years and care must be taken when comparing dispersant effectiveness tests conducted on these oils that span many years. Only five of the test programs evaluated dispersant effectiveness on specific North Slope production crudes (Endicott, Northstar and Pt. McIntyre). These oils were used in projects that were conducted for BSEE's predecessor, the Minerals Management Service (MMS), with oils sourced by them specifically for cold water dispersant effectiveness testing. These oils are possibly more representative of the type of crude that might be spilled in the Beaufort and Chukchi Seas. As new oils come into production in the waters of the Beaufort and Chukchi Seas they should be evaluated for their potential for chemical dispersion under the range of environmental conditions they might be spilled in.

5.5 Dispersant Type

Most of the dispersant effectiveness tests on Alaskan oils identified in Table 5-2 used one or both of Corexit 9500 and Corexit 9527 in their testing. This is not surprising since these brands have been the most stockpiled products in North America and have been on the market for many years. Other dispersants tested on ANS crude under a variety of conditions include Archochem D609, Atlantol AT-7, BP 1100WD, Citrikleen, Corexit 9550, Dispersit SPC1000, Dispolene 34S, Dasic Fresh Water, Dasic Slickgone NS, Enersperse 700, Enersoerse 1037, Finasol OSR 5, Finasol OSR 7, Finasol OSR 51, Finasol OSR 52, Inipol IP90, Inipol IPF, Inipol PC, OFC D-609, Slickgone NS, and Superdispersant 25. Many of these products are no longer commercially available or on the US EPA NCP list of approved products for US waters. The significance of dispersant type will be discussed more fully when addressing the other variables that are specific to Arctic dispersant use (cold temperatures, salinity, mixing energy and ice). If new chemical formulations are developed or 'green' dispersants are developed their effectiveness on the crude oils currently being produced on the North Slope should be tested using bench and large scale test methods.

5.6 Water Temperature

There is concern in temperate or subarctic climates that temperature, per se, is a problem in dispersant effectiveness, and that dispersants should not or cannot be used in cold climates. This concern is generally unfounded, except in the case of so-called "high pour point oils", some of which can become semi-solid at temperatures well above freezing. Reduced temperature simply increases the viscosity of the dispersant product and the spilled oil. Dispersant products can be formulated to be non-viscous in cold temperatures, so this is not a problem. The viscosity of the spilled oil will become higher at low temperatures, but perhaps not too high for effective chemical dispersion. In early work by Mackay (1979), that used the Mackay Nadeau and Steelman (MNS) test and a hoop tank, it was concluded that the primary effect of water temperature was to lower the oil temperature and increase the oil viscosity which in turn reduced the dispersant effectiveness. In later work where Prudhoe Bay crude oil was used, Mackay (1986) concluded that "There is no inherent reason to suggest that cold climate dispersion is significantly less feasible than temperate dispersion" and that "dispersion is likely to require more dispersant under these cold conditions but the extra amount is unlikely to be large except when the oils are unusually viscous, close to their pour point or waxy". Tests conducted using

the ExxonMobil dispersant effectiveness test (EXDET) by Mackay (1995) found a slight **decrease** in effectiveness of C 9527 on ANS crude as the temperature **increased** from 4.4 °C to 15.5 °C. Byford et al (1983) found in Warren Spring Laboratory tests (WSL) and tank tests, that included North Slope Crude oil conducted at 0 and 10 °C, that in all cases the dispersant performance was not reduced in the lower temperatures and in some cases was enhanced. Moles et al (2001, 2002) found that dispersant effectiveness, as measured by the swirling flask test (SFT), on fresh ANS was below the detectable limits when the water temperature was 3 °C. They also found that the effectiveness of Corexit 9500 was similar at 10 and 22 °C in 32 ppt salt water but lower effectiveness was measured in the cold condition for Corexit 9527. Chandrasekar et al (2005, 2006) found that the best dispersion of ANS was achieved in the baffled flask test (BFT) at 22 °C with a reduction in effectiveness at both 5°C and 35 °C. Fingas et al (2006) found that Corexit 9500 was equally effective in the SFT test on ANS crude at temperatures between 5 to 10 °C and **decreased** when the temperature **increased** to 25 °C. In a study using Alberta Sweet Mixed Blend crude oil and the SFT test Fingas et al (2005b) found a similar trend with similar effectiveness at 5 to 20 °C and a reduction in effectiveness at 25 °C. Earlier work with the SFT test by Fingas et al (1991) found a reduction in dispersant effectiveness when temperatures were lowered from 50 °C to 0 °C. Large scale tests conducted in cold water conditions (-2.8 to 3.3°C) at the Ohmsett facility (SL Ross 2002, 2003, 2006, 2006b) resulted in near complete dispersion (74 to 99%) of fresh ANS, Endicott, Northstar and Pt. McIntyre crude oils. The weathered and emulsified oils were not as easily dispersed in a number of the tests with measured effectiveness ranging from 3 to 35%.

Crude oils that are relatively non-viscous and whose viscosities do not increase to very high values when temperatures are lowered to 0° C are likely to be chemically dispersible over the full range of possible water temperatures. On the other hand, fresh or weathered oils that are relatively viscous to begin with, but yet dispersible at high temperatures, may become excessively viscous and un-dispersible when lowered to freezing temperatures. The main lesson here is that it is the viscosity of the oil at the water temperature in which it is spilled that is the key factor in deciding dispersant effectiveness and not the temperature per se. This points to the need to fully understand the fresh and weathered oil viscosities of the specific oils that are likely to spilled in cold waters. This is accomplished through laboratory testing and modelling. Once such analysis is done, it should become evident if a specific oil is a good candidate for dispersant

use or not. From the past testing that has been conducted on Alaskan oils it appears that the Alaskan oils produced to date are generally dispersible at cold temperatures when fresh and slightly weathered but may not be readily dispersed when heavily weathered and emulsified. Additional cold water testing of the chemical dispersibility of specific Alaskan oils when weathered and emulsified may be useful to further define the time window of opportunity for the successful dispersion of these oils under typical conditions that could be encountered in the study region.

5.7 Water Salinity

An extensive review of worldwide scientific and technical journals was undertaken for the US Department of Interior (SL Ross 2010) to identify relevant literature on the use of chemical treating agents for oil spill response in fresh and brackish water. This review found that numerous laboratory-scale, meso-scale and field studies, dating back to the late seventies, have been conducted to study the effect of water salinity on the effectiveness of oil spill chemical dispersants on a range of oils. The consistent significant finding of all of these tests is that dispersant designed for use in marine environments (30 to 35 ppt salinity) are considerably less effective when the salinity falls below about 20 ppt or above 40 ppt. Of the dispersants most commonly used in US waters, Corexit 9500 has been shown to be more effective than Corexit 9527 in lower salinity waters.

Dispersants have been formulated for use in fresh water and these have also been tested for effectiveness over a range of water salinities, although not as extensively as the marine dispersants. The effectiveness of the freshwater dispersants have been shown to generally be much better than the marine products in freshwater but often achieve their best results in waters between 10 and 20 ppt salinity.

Most of the research identified in Table 5-2 where salinity was varied in the test matrix form part of the previous review described above (SL Ross 2010). Table 5-2 references identify research that was specific to Alaskan crude oils (exclusively Alaska North Slope blend or Prudhoe Bay crude). The effectiveness of dispersants on the Alaskan oil under varying water salinities generally is consistent with the findings for other crude oils. The work by Chandrasekar et al (2006) and Nagaraja et al (2008) were not part of the 2010 review. It is interesting to note that in the work reported by Chandrasekar and Nagaraja that the effectiveness of dispersant A

(assumed to be Corexit 9500 based on previous reports by this author) on ANS crude in the BFT varied by less than 15% over the salinity range (from 10 to 34 ppt) and temperature range tested (5 to 35 °C). These tests showed greater effectiveness of a marine dispersant (Corexit 9500) on ANS crude at low water salinity than has been demonstrated by many other test programs. This improvement may be due to the higher energy level imparted in the BFT when compared to the SFT which was used in many of the other tests that investigated the dispersibility of ANS crude at different temperatures and salinities. The work conducted by Abbasova (2005) also show high dispersibility of a Caspian crude oil in low salinity water (12ppt) using the BFT. In early work by Cox and Shultz (1981) using the MNS test apparatus, no difference in dispersant effectiveness was identified over salinities ranging from 10 to 32 ppt. Unfortunately the dispersants used in these tests were not identified by brand name.

The water salinities in the US Beaufort and Chukchi Seas are generally greater than 20 ppt, even during the spring ice melt season, with the exception of fresh water outflows inside the barrier islands of the US Beaufort Sea and isolated near shore regions of the Chukchi Sea (see Task 1 Report). Additional testing of Alaskan oils in low salinity water may be a low priority since chemical dispersants designed for marine use have been shown to generally be effective on most oils and specifically on ANS crude oil in waters with salinities 20 ppt and greater. If new 'green dispersants' are developed and proposed for Arctic use their effectiveness in water salinities ranging from 15 to 35 ppt should be evaluated on Alaskan oils.

5.8 Mixing Energy

Mixing energy is of obvious importance to the dispersion of marine oil spills: simply put, the more mixing the better. Oil slicks can be broken up into small droplets and disperse naturally under high energy conditions but much more rapid dispersion and dispersion under much less vigorous wave energies can be accomplished by applying chemical dispersants as described in Section 2 above. The bench-scale, and meso-scale laboratory tests and outdoor wave tanks all impart a slightly different mixing energy to the oil-water-dispersant system and thus can result in different dispersant effectiveness estimates for a given oil and dispersant combination. A comparison of dispersant effectiveness estimates using identical oils and dispersants was made for the swirling flask test (SFT), baffled flask test (BFT), ExxonMobil dispersant effectiveness test (EXDET), the Warren Spring Laboratory test (WSL), and Ohmsett test tank (SL Ross 2011).

Based on the results of this study it can be assumed that the mixing energy rankings for these tests fall into the following pattern: SFT<BFT<EXDET<Ohmsett. Clark et al (2005) found a similar relationship in their comparison of small-scale DE test results: SFT< EXDET <BFT=WSL. Numerous other studies have compared small scale test results from different test apparatus and have directly measured the energy present in the various test apparatus. The issue of wave energy and dispersant effectiveness is universal to both warm and cold climate conditions and a complete discussion of this issue is beyond the scope of this review. The issue is mentioned only to highlight the fact that results from one set of tests using one apparatus and test method may not give the same results or trends as those from another method. This may be one of the reasons for the somewhat inconsistent results that have been reported for dispersant effectiveness as a function of temperature and salinity discussed above. Of more importance to this document is the effect that the presence of ice has on the level of energy available for the chemical dispersion of oil. The attenuation of waves and surface energy by floating ice is a well-known phenomenon and the higher the ice concentration the more the waves are dampened. The influence of ice on the dispersion process is discussed under a separate heading below.

5.9 Effect of Ice on Dispersant Effectiveness

There have been a limited number of dispersant effectiveness studies where ice has been present during the test and even fewer where Alaskan oils have been tested. Dispersant effectiveness in ice was studied by Mackay et al. 1979; Cox and Shultz 1981; Byford et al. 1983; Brown et al. 1985; and Brown and Goodman 1996, SL Ross 2002, Owens 2004, Spring et al 2006, Sorstrom et al 2010. The work here ranged from experiments in small containers, to medium sized-tank experiments, to experiments at a large wave basin in Calgary, at the Ohmsett facility and in one field trial. Of these studies only those by Owens and SL Ross used Alaskan oils.

In the small-scale tests conducted by Cox and Shultz and Byford the presence of ice with a surface coverage of between 20 and 50% generally increased the chemical dispersion of the oil. This was speculated to be due to the result of the pumping action of the broken ice pieces. Brown et al 1985 also measured higher dispersion rates than achieved in similar open water conditions in tests where both slush and broken ice were present. Tests in the Ohmsett facility (SL Ross 2002) with fresh and weathered (10% evaporative loss) ANS crude conducted in 80% ice cover resulted in greater than 95% dispersion. The measured dispersant effectiveness (DE) values for ANS weathered to 20% loss were 54% in 8/10th ice, 30% in 4/10th ice and 22% in open water.

All of these tests were conducted in non-breaking wave, low energy swells. Chemical dispersion was enhanced by the presence of ice in these tests. The increased dispersion over open water conditions was attributed to the pumping action or turbulence caused by the movement of the ice pieces in the swell. Owens et al (2004) reported similar improvement over open water conditions in the chemical dispersion of ANS crude oil when brash ice was present in 4/10 and 8/10 coverage.

The presence of ice has been shown to improve the chemical dispersion of oil in low energy conditions by a number of studies. Successful dispersion of fresh and evaporated ANS in ice appears to be possible in lower wave energies than would normally disperse oil in open water conditions due to the additional turbulence caused by the moving ice. Some movement of the broken ice is necessary to generate the dispersion.

Ship propeller wash and water jets have been shown to be effective in dispersing oil that has been treated with dispersant in a broken ice system in the absence of any natural mixing. This was demonstrated in meso-scale tests and in a wave basin (Nedwed et al 2007, Spring et al 2006) and in the field (Sorstrom et al 2010). Oil treated by dispersant in a solid or 80+% ice cover was effectively dispersed in all of these tests using ice-breaking, ship propeller wash and water jets. In all cases the droplet sizes generated were very small and the droplets remained suspended in the water for long periods.

Table 5-2 Chemical Dispersant Research on Alaskan Oil: Summary Table

Research Paper	Oil	Dispersant	Test Method[1]	Parameters Varied in Tests[2]			
				Temp	Salinity	Energy	Ice
Abbasova, A. et al. 2005	Chirag crude oil (Caspian Sea)	Finasol OSR51, Superdispersant 25, Corexit EC 9527a, Corexit EC 9500a, Slickgone NS, Inipol IP90	BF	X	X	X	O
Anderson, J.W., D.L. McQuerry, S.L. Kiesser. 1985.	Alaska North Slope	14 dispersants	MNS	X	X	X	O
Belore, R. 2003.	fresh and weathered Hibernia and ANS crude oils	Corexit 9500 and 9527	Ohmsett wave tank	X	X	X	O
Belore, R., S. Ross. 2000	Alaskan North Slope crude	Corexit 9500 and 9527	SLR wave tank	X	X	X	O
Blondina, G., M Singer, I. Lee, M. Ouano, M. Hodgins, R. Tjeerdema. 1999.	Prudhoe bay crude plus various others	9500 & 9527	SF	X	√	X	O
Brandvik, P.J., 0.0. Knudsen, M.O. Moldestad and P.S. Dating, 1995.	Norwegian Oils Only	Inipol IPF, Inipol PC, Enersperse 700, Finasol OSR-52, Dasic Fresh Water, 9500 & 9527 + others	IFP	X	√	X	O
Brown, H.M., D.K.Weiss, R.H. Goodman. 1990	North Slope & Drift River crude	Corexit 9550 or 9527	Esso Wave Tank	X	X	X	O
Brown et al. 1985	Federated crude (ASMB)	Corexit 9527 & CRX-8	Esso Wave Tank	X	X	X	X

Research Paper	Oil	Dispersant	Test Method[1]	Parameters Varied in Tests[2]			
				Temp	Salinity	Energy	Ice
Brown, H.M., R.H. Goodman. 1987	ANS	9527, 9550, Enersperse 700	Esso Wave Tank	X	X	√	O
Brown and Goodman 1996.	Federated crude (ASMB)	Corexit 9500 and Corexit 9527	Esso Wave Tank	X	X	√	√
Byford, D., P. Green, A. Lewis. 1983	Lago Medio, North Slope Crude, Medium Fuel Oil	Corexit 9527, Corexit 9550 BP1100WD, Fiansol OSR5, Dispolene 34S, Arcochem D609	WSL, BP Wave Tank	√	√	X	X
Chandrasekar, S. G.A., Sorial, J.W. Weaver. 2003.	Prudhoe Bay South Louisiana crude and #2 Fuel oil	Corexit 9500 and Dispersit-SPC 1000	BF	√	X	√	O
Chandrasekar, S.; Sorial, G.A.; Weaver, J.W. 2006.	Alaskan Prudhoe Bay, South Louisiana crude oil, No. 2 Fuel Oil (fresh & weathered)	Corexit 9500 and Dispersit-SPC 1000	BF	√	√	√	O
Cox, J., L. Shultz 1981	Sadlerochit crude fresh, 10 and 30% weatehred, 10% weathered Arctic diesel, 10% weathered Kuparuk crude	X, Y, Z	MNS, Hoop Tank	X	X	√	√
Fingas, M., B. Fieldhouse, Z. Wang. 2006.	ANS	Corexit 9500 and 9527	SF	√	√	X	O
Fingas, M., B.Fieldhouse, Z.Wang. 2005b	ASMB	Corexit 9500	SF	√	√	X	O

Research Paper	Oil	Dispersant	Test Method[1]	Parameters Varied in Tests[2]			
				Temp	Salinity	Energy	Ice
Fingas, M., L. Ka'aihue. 2005a	Various including ANS	various	various	√	√	√	O
Fingas, M.F., I. Bier, M. Bobra and S. Callaghan. 1991	ASMB, Norman Wells, Adgo	Corexit 9527, Enersperse 700 and Citrikleen	SF	√	√	X	O
Fiocco, R.J., P.S. Daling, G. DeMarco, R.R. Lessard, 1999.	Alaska North Slope	Corexit 9500	MNS, WSL	X	X	√	O
George-Ares, A., R.R. Lessard, K.W. Becker, G.P. Canevari and R.J. Fiocco,	ANS + 3 other non-Alaskan oils	Corexit 9500, calcium chloride modified 9500, Dasic freshwater, Enersperse 1037, Inipol IPF	EXDET	X	√	X	O
Lewis, A.; Crosbie, A.; Davies, L.; Lunel, T. 1998.	Forties Blend, Alaskan North Slope crude, and IFO-180 fuel oil	Corexit 9500 and Dasic Slickgone NS	Field test	X	X	√	O
Li, Z., K. Lee, T. King, M. Boufadel, A. Venosa. 2009.	ANS and Mesa crude	Corexit 9500 & Dispersit-SPC 1000	EPA / DFO wave tank	X	X	√	O
Mackay, D. , R. Mascarenhas, K. Hossain, T. McGee. 1979	Alberta Mixed Blend (ASMB), Lago Medio	9527	MNS, Hoop, CSSA	√	X	√	X
Mackay, D. 1995.	Alaskan North Slope crude	Corexit 9527	MNS, WSL, Exdet,Esso Wave Tank	√	√	√	O
Mackay, D., Chau, Y. Poon. 1986	Prudhoe Bay Crude and various others	9527, 9550, BPMA700	MNS, Hoop, RF,Bobra	√	√	√	O

Research Paper	Oil	Dispersant	Test Method[1]	Parameters Varied in Tests[2]			
				Temp	Salinity	Energy	Ice
McAuliffe, C.D. et al. 1981.	Alaskan Prudhoe Bay crude oil	Code Named H & J	Field	X	X	√	O
Moles, A., L. Holland, J. Short. 2002	ANS	9500 & 9527	SF	√	√	X	O
Moles, A.L. Holland, J. Short, 2001	ANS	9500 & 9527	SF	√	√	X	O
Nagarajan, K., N. Deshpande, G. Sorial, J. Weaver. 2008.	Alaskan Prudhoe Bay, South Louisiana crude oil, No. 2 Fuel Oil (fresh & weathered)	Corexit 9500 (A) & Dispersit-SPC 1000 (B)	BF	√	√	√	O
Nedwed, T. , R. Belore, W. Spring, D. Blanchet. 2007	Chayvo Z6	Corexit 9527	SL Ross Wave Tank, AKER Ice Basin (prop wash)	X	X	√	√
Owens, C.K.R. Belore, 2004.	Alaska North Slope, Hibernia, Chayvo	Corexit 9527	Ohmsett	X	X	√	√
Payne, J.R. et al. 1985	Alaskan Prudhoe Bay crude oil	Corexit 9550, Finasol OSR-7, EC. O ATLANT'TOL AT-7, and OFC D-609	Old EPA protocol	√	√	X	O
SL Ross, MAR Inc. 2003	ANS, Endicott, Northstar, Middle Ground Shoal & Pt. McIntyre (fresh and weathered)	Corexit 9527	SLR Wave Tank & Ohmsett	X	X	√	O
SL Ross, MAR Inc. 2006	ANS, Endicott, Northstar & Pt. McIntyre (fresh and weathered)	Corexit 9527	SLR Wave Tank & Ohmsett	X	X	√	O

Research Paper	Oil	Dispersant	Test Method[1]	Parameters Varied in Tests[2]			
				Temp	Salinity	Energy	Ice
SL Ross, MAR Inc. 2009	ANS, Endicott, Oseberg, Rock, Ewing Bank, IFO 30	Corexit 9500	SLR Wave Tank & Ohmsett	X	X	√	O
SL Ross. 2002.	Alaska North Slope and Hibernia (fresh and weathered)	Corexit 9500 & 9527	Ohmsett	X	X	√	√
SL Ross. 2006.	fresh, air sparged and emulsions of Endicott, IFO 30, IFO 120 and Sockeye crude	Corexit 9500 & 9527	SLR Wave Tank & Ohmsett	X	X	√	O
SL Ross. 2010. (lit review)	Various including ANS	various	various	X	√	X	O
SL Ross. 2011	Endicott, ANS plus 12 other crude oils	Corexit 9500	Ohmsett, WSL, BF,SF,Exdet	X	X	√	O
Smith, D., G. Holliday. 1979	ANS	H & J	Field tests	X	X	√	O
Spring, W, T. Nedwed, R. Belore.2006	Chayvo Z6	Corexit 9527	SL Ross wave tank & AKER wave basin (prop wash)	X	X	√	√
Sorial, G.A.K.M. Karen, H. Edith, A.D. Venosa, D.W. King. 2001.	Alaskan Prudhoe Bay and South Louisiana crude	18 Different Products	SFT & BF	X	X	√	O
Sørstrøm, S.E., Per Johan Brandvik, I. Buist, P. Daling, D. Dickins, L. Faksness, S.Potter, J. Rasmussen and I. Singsaas.2010.	Troll B crude	Corexit 9500	Field test	X	X	√	√

Research Paper	Oil	Dispersant	Test Method[1]	Parameters Varied in Tests[2]			
				Temp	Salinity	Energy	Ice
Strom-Kristiansen, T., P.S. Daling, A. Lewis, A.B. Nordvik. 1994.	ANS plus Brent Blend, Murban and Bonny Light	9527, 9554, Enersperse 700,Several others	MNS, IFP, WSL	X	X	√	O
Venosa, A.D.G.A. Sorial, D.W. King. 2001	ANS and South Louisiana Crude	Six – test results not tied to dispersant brand	BFT	X	X	X	O
Venosa, A., K. Lee, M. Boufadel, Z. Li, E. Wickley-Olsen, T. King, 2008	ANS & Mesa light	Corexit 9500 and Dispersit SPC 1000	EPA/DFO wave tank	X	X	√	O
White, D.M.; Ask, I.; Behr-Andres, C. 1999.	Alaska North Slope	Corexit 9500	Modified SFT & EXDET	X	X	√	O
Wrenn, B., A. Virkus, B. Mukherjee, A. Venosa. 2009.	Mars crude	Various experimental formulations	BF	X	X	X	O

[1]RF- Rotating Flask, MNS- Mackay Nadeau Steelman test, Bobra- double tube test, SFT- Swirling Flask, BFT- EPA Baffled Flask Test, IFP- French dilution tests, WSL-Warren Spring Laboratory rotating flask, EXDET- ExxonMobil Dispersant Effectiveness Test

[2]O – parameter not tested, √ parameter varied in test, X parameter not varied.

6 Identification of Knowledge Gaps

The results of the review of past dispersant effectiveness testing on Alaskan oils (section 5) and the environmental conditions in the US Chukchi and Beaufort Seas relevant to chemical dispersion (chapter 4) are discussed in this section with the goal of identifying gaps in our understanding of the potential effectiveness of dispersants in these regions.

6.1 Water temperature

The dispersibility of a crude oil is a strong function of its viscosity, which in turn is often very temperature dependent. The surface water temperatures in the Chukchi and Beaufort Seas in the open water seasons can vary from close to freezing (-2 °C) to upwards of 14 °C with considerable spatial variability in both regions. As crude oils cool their viscosities increase and with increasing viscosities there is a potential for the reduction of dispersant effectiveness. If the water temperature is below the pour point of the oil and the oil is no longer fluid the oil will also not be amenable to chemical dispersion because the dispersant cannot easily mix with the oil. There is really no water temperature that will completely restrict the use of chemical dispersant. The main lesson here is that it is the viscosity of the oil at the water temperature in which it is spilled that is the key factor in deciding dispersant effectiveness and not the temperature per se. The oil viscosity – temperature relationship must be considered for each candidate oil before an evaluation of the potential for dispersant effectiveness can be made. From the past testing that has been conducted on Alaskan oils it appears that the Alaskan oils produced to date are generally dispersible at cold temperatures when fresh and slightly weathered but may not be readily dispersed when heavily weathered and emulsified. Additional cold water testing of the chemical dispersibility of specific Alaskan oils when weathered and emulsified may be useful to further define the time window of opportunity for the successful dispersion of these oils under typical conditions that could be encountered in the study region.

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6.2 Water Salinity

Most of the past DE tests on crude oils in general and Alaskan oils specifically have shown that dispersant designed for use in marine environments (30 to 35 ppt salinity) are considerably less effective when the water salinity falls below about 20 ppt or above 40 ppt. However, the effectiveness of a dispersant on both ANS crude and a Caspian crude oil in the baffled flask test (BFT) showed considerably higher dispersibility at low water salinities (10 to 15 ppt) than has been demonstrated in many other test programs. This improvement may be due to the higher energy level imparted in the BFT when compared to the SFT which was used in many of the other tests that investigated the dispersibility of ANS crude at different temperatures and salinities.

With the exception of isolated near shore fresh water outlets there is minimal variation (between 28 and 34 ppt), both temporally and spatially, in surface water salinity throughout the U.S. Chukchi and Beaufort Sea regions. This offshore salinity variation is well within the optimal effectiveness range for marine chemical dispersants.

Water salinities in the nearshore area of the Beaufort Sea can be considerably lower than the offshore areas for short periods of the year due to the influence of fresh water river outflows and ice melt. Fresh water from river outflow can form a 1 to 2 m deep lens under the landfast ice that may extend up to 25 km offshore from the major river mouths. The surface water salinities in these areas approach that of fresh water during the early ice breakup period and prior to the mixing of the upper and lower water layers by strong winds and waves. The presence of this near shore fresh water during this period could hinder the effectiveness of chemical dispersants. Additional work on the effectiveness of dispersants over a range of salinities under realistic breaking wave conditions may be warranted to further investigate their potential for these near shore fresh water outflow regions.

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6.3 Presence of Ice

There have been a limited number of dispersant effectiveness studies where ice has been present during the test and even fewer where Alaskan oils have been tested. The presence of ice has been shown to improve the chemical dispersion of oil in low energy conditions. Successful dispersion of fresh and evaporated ANS in ice appears to be possible in lower wave energies than would normally disperse oil in open water conditions due to the additional turbulence caused by the moving ice. Ship propeller wash and water jets have been shown to be effective in dispersing oil that has been treated with dispersant in a solid or 80+% ice cover in the absence of any natural mixing. In these cases the drop sizes generated were very small and the drops remained suspended in the water for long periods.

In the Chukchi Sea region open water periods where conventional aerial application methods could be used generally exist only in the months from June through November. Open water is most common in the months of July through October in this region but the shoulder months of June and November may present dispersant application opportunities depending on the ice year. In the Beaufort Sea region the maximum likely extent for open water dispersant use is from July to October with the more likely season being from August to October. The remainder of the year will see short transition periods from open water to complete (90+ %) ice cover which will affect conventional dispersant use. In ice conditions with less than 3/10ths cover chemical dispersants will perform much the same as in open water conditions since the surface mixing energy is not overly dampened by the presence of the ice. The presence of greater than 9/10ths ice either encapsulates the oil making it impossible to target with aerial applied dispersant or dampens the surface energy such that there is insufficient energy to break the oil into droplets once treated The performance of dispersants in 3/10ths to 8/10ths ice cover without additional mixing energy applied is somewhat uncertain and requires additional study. Additional research on the potential for dispersant use under partial ice cover conditions is currently underway (OGP 2014, BSEE 2014).

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6.4 Wave Energy

An assessment of hindcast historical wind data and a correlation between wind speeds and wave energy was used to identify the percentage of time that aerial dispersant operations could be viable in section 5, both from a spray application efficiency standpoint and the presence of sufficient wave energy for oil dispersion. Based on this assessment chemical dispersant use would be favorable for 80 to 90% of the time in the two regions. This does not account for other operational limitations such as visibility and daylight hours as this was out of the scope of the study. Based on this assessment wind speeds and wave heights in the region should not generally be an impediment to chemical dispersant use.

Mixing energy is of obvious importance to the dispersion of marine oil spills with more mixing being better. Oil slicks can be broken up into small droplets and disperse naturally under high energy conditions but much more rapid dispersion and dispersion under much less vigorous wave energies can be accomplished by applying chemical dispersants. The bench-scale, and meso-scale laboratory tests and outdoor wave tanks all impart a slightly different mixing energy to the oil-water-dispersant system and thus can result in different dispersant effectiveness estimates for a given oil, dispersant water salinity, temperature combination. A comparison of dispersant effectiveness estimates for the swirling flask test (SFT), baffled flask test (BFT), ExxonMobil dispersant effectiveness test (EXDET), the Warren Spring Laboratory test (WSL), and Ohmsett test tank ranks the energy for these tests into the following pattern: SFT<BFT=WSL<EXDET<Ohmsett. The issue is mentioned only to highlight the fact that results from one set of tests using one apparatus and test method may not give the same results or trends as those from another method. This may be one of the reasons for the somewhat inconsistent results that have been reported for dispersant effectiveness as a function of temperature and salinity discussed above. It is always preferable to test dispersants under the most realistic conditions possible but this is not always possible due to permitting requirements for field trials or costs associated with large tank tests. Additional DE testing on Alaskan oils using realistic breaking wave conditions and varying environmental conditions would be useful to solidify our understanding of the potential for chemical dispersants.

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6.5 Alaskan Oil Types

At the present time the only oils being produced and transported (by pipeline to shore) in the Beaufort and Chukchi Seas are Northstar and Endicott crude oils and are the only crude oils that could be spilled directly into Alaskan offshore waters from present production fields. No oils are presently being produced in Chukchi Sea waters. Alaska North Slope Crude (ANS), or Prudhoe Bay crude as it was named in early test programs, has been the Alaskan oil of choice for most of the dispersant effectiveness tests conducted on Alaskan oils. Only five of the test programs evaluated dispersant effectiveness on specific North Slope production crudes (Endicott, Northstar and Pt. McIntyre). These oils were used in projects that were conducted for MMS with oils sourced by them specifically for cold water dispersant effectiveness testing. These oils are possibly more representative of the type of crude that might be spilled in the Beaufort and Chukchi Seas. As new oils come into production in the waters of the Beaufort and Chukchi Seas they should be evaluated for their potential for chemical dispersion under the range of environmental conditions they might be spilled in.

6.6 Dispersant Types Tested

Most of the dispersant effectiveness tests on Alaskan oils identified in Table 5-2 used one or both of Corexit 9500 and Corexit 9527 in their testing. This is not surprising since these brands have been the most stockpiled products in North America and have been on the market for many years. More wide spread testing of additional National Contingency Plan Listed dispersants on Alaskan oils under realistic conditions would provide spill responders with important information concerning the potential use of other products in this environment.

7 Meso-Scale Tank Tests

After discussion with the a technical representative from BSEE, a suite of DE tests using the SL Ross wind-wave tank on four Alaskan crude oils with four water salinities were selected for additional study to shed more light on the effectiveness of marine dispersants over a range of water salinities under high energy breaking wave conditions.

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7.1 Oils and Dispersant Used in Test Program

Four Alaskan crude oils were used in the test program. The oils and their basic fresh and weathered oil physical properties are shown in Table 7-1. The second column in Table 7-1 shows the degree of weathering that each of the oils received to achieve the weathered oil properties shown. The densities and viscosities reported in Table 7-1 were measured by SL Ross during the course of the current project. The modeling constants used to estimate volume percent evaporation as a function of oil density shown in the last four columns of the table are from previous oil analyses conducted on the test oils (SL Ross, MAR, DF Dickins, 2008).

Table 7-1 Test Oil Properties

Oil Name	Degree of Weathering (% loss by mass)	Density (kg/m^3 @ 10 °C)		Viscosity (cP @ 10 °C & 100 s^{-1})			Evaporation Modeling Constants			
		Fresh	Weathered	Fresh	Weathered	Weathered & Emulsified (50% water content)	Standard density (kg/m^3)	Standard density temperature (°C)	Density Constant #1	Density Constant #2
Endicott	6.0	0.924	0.935	340	1030	2370 to 3380	920.8	288.7	59.0	0.7736
Kuparuk	13.1	0.923	0.951	124	970	2050 to 4400	920.5	288.7	169.9	0.585
Northstar	43.1	0.823	0.869	1	20	not applicable	820.7	288.7	104.3	0.804
ANS Blend	21.4	0.879	0.940	19	1230	4000 to 5000	869.3	288.7	163.2	0.635

7.2 Test Methods and Equipment

All tests were conducted in the SL Ross wave tank shown in Figure 7-1. This tank is 10 m long by 1.3 m wide by 1.2 m deep and is fitted with a computer controlled wave paddle and energy dissipating beach. The tank is fitted with a cooling coil that permits the maintenance of the water at temperatures down to near freezing conditions. The tank was operated with a 20 cm breaking wave (trough to crest) that was programmed to break in the oil slick every 30 seconds. Tests were run for 15 minutes. Oil was held within the wave breaking zone using an air bubble barrier. Dispersant effectiveness was quantified by collecting the surface oil remaining at the end of each

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test to determine the percentage of oil dispersed and by measuring the dispersed oil drop size distributions using a LISST particle size analyzer placed 40 cm below the water surface in the center of the bubble barrier containment zone.

Figure 7-1 SL Ross Wave Tank

For the fresh and weathered oil tests approximately 750 ml of oil was placed into a container, weighed, emptied onto the water surface inside the containment area and the empty container re-weighed to determine the mass of oil discharged. Dispersant was applied using an air pressure powered sprayer fitted with a Spraying Systems Company flat fan nozzle (800015) operated at 50 psi. The dispersant sprayer is shown in Figure 7-2. The quantity of dispersant needed to achieve a 1:20 dose rate (by mass) was loaded into the sprayer prior to application and the full quantity of dispersant was applied to the surface of the oil. This dose rate was used as it is the manufacturer's recommended dosage for general use. The dose rate was not changed in the study so comparisons of dispersant effectiveness with varying water salinities could be made with all other conditions kept constant. For the weathered and emulsified oil tests 500 ml of weathered oil was mixed with 500 ml of salt water of the same salinity as the water of the test being

conducted. The oil and water were mixed for 8 minutes using the paint stirrer shown in Figure 7-3. This method for realistic emulsion generation was developed in a previous study for the US Department of the Interior (SL Ross 2005). The dispersant dose used in the emulsion tests was again 1:20 based on the total mass of the oil and water mixture spilled.

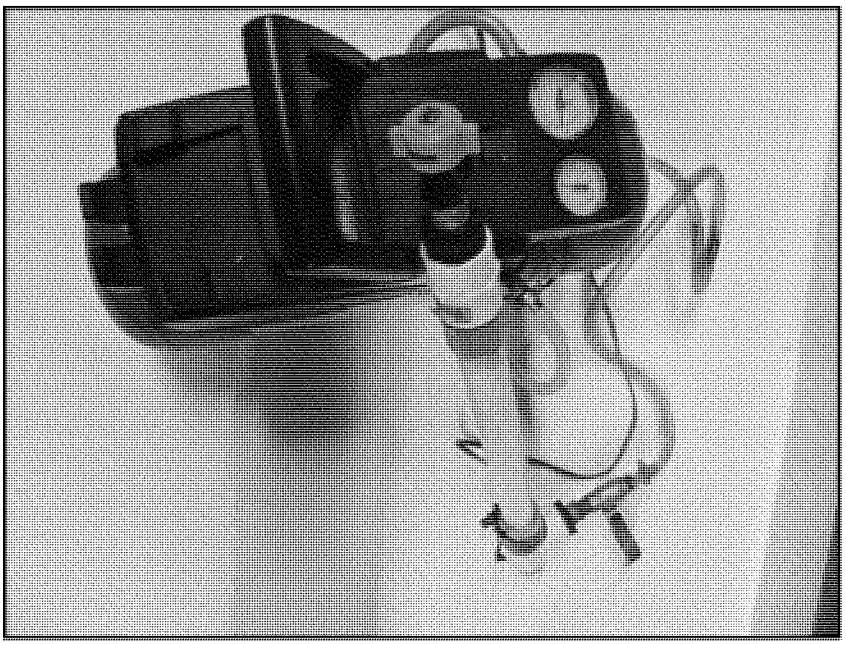

Figure 7-2 Dispersant Applicator

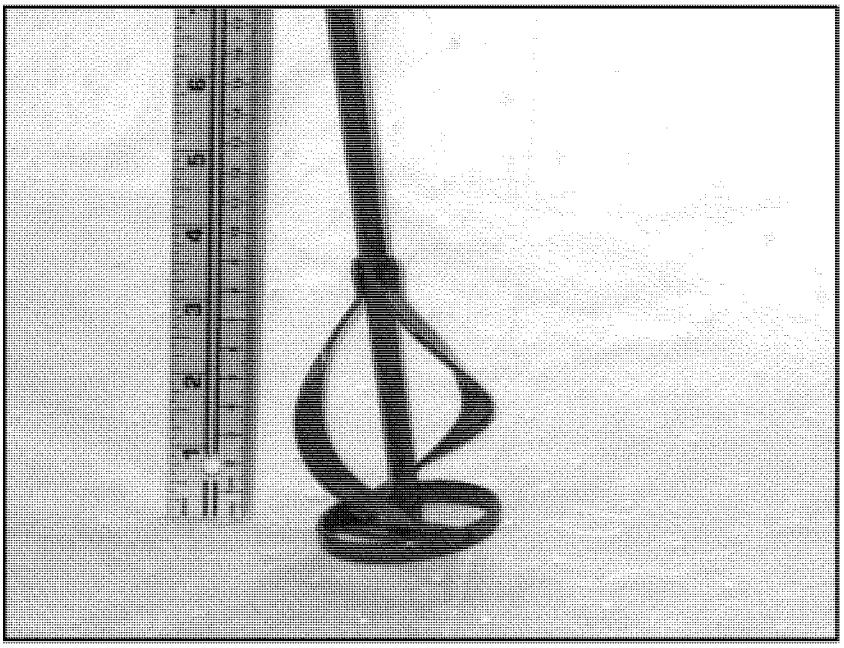

Figure 7-3 Emulsion Mixer

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7.3 Test Variables and Test Matrix

Corexit 9500 was used in all tests. To keep the test matrix at a manageable level only one dispersant to oil ratio was investigated for each type/weathered state of oil. A 1:20 DOR was used in all tests so a comparison of dispersant effectiveness as a function of water salinity could be made.

Alaska North Slope crude (provided by BSEE), Endicott, Northstar and Kuparuk crude oil (from SL Ross supply) were used in the testing. Tests were conducted on fresh, evaporated and evaporated plus emulsified crude oils (3 weathered states in total). Northstar does not form a stable emulsion so tests could not be conducted on emulsions of this oil. Emulsions were generated using the experience and techniques developed during earlier projects funded by the US Mineral Management Service that identified realistic water-in-oil emulsion making methods (SL Ross & A. Lewis, 2005). Tests were conducted in water with salinities of 5, 10, 20 and 30 ppt. All tests were conducted with a water temperature of 10 °C.

7.4 Results

7.4.1 Dispersant Effectiveness (DE) Estimates

The oil collected from within the containment zone at the end of each 15 minute SL Ross wave tank test was treated with a small amount of emulsion breaker (Alcopol) and placed in a heated bath and for several hours to facilitate removal of any water. The density of the oil was then measured to allow the estimation of oil loss through evaporation using the modeling constants provided in Table 7-1. This was important for the fresh oils and the lighter Northstar crude in particular. After accounting for evaporative losses the percent of oil lost to the water column, or a raw estimate of percent dispersed, without any adjustment for oil drop size, was calculated for each test. The dispersant effectiveness estimates presented in this section do not take into account the quality of the dispersion as measured by the oil drop size distribution in the dispersion. The results for the unadjusted dispersant effectiveness (DE_{raw}) estimates are presented in Figure 7-4 (Endicott), Figure 7-5 (Kuparuk), Figure 7-6 (Northstar) and Figure 7-7 (ANS). The DE_{raw} values reported in these figures reflect the oil lost from the surface of the containment area over the duration of the test. The complicated beaches in this test tank make it

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impractical to collect any oil that resurfaces outside of the containment zone at the end of the test. It is likely that some portion of the oil entrained by breaking waves during the test is in the form of large droplets that escape the bubble barrier system at depth, are only temporarily dispersed or entrained and then rise to the surface outside of the containment zone. This will not occur in all tests and the extent of this will be a direct function of the dispersed oil drop size distributions and depth of the dispersions generated. The DE_{raw} values reported in this section reflect the maximum possible DE that can be expected for the oil and water salinity combinations tested. A second dispersant effectiveness that accounts for the oil drop size distribution measured, and is a more realistic indication of dispersant effectiveness in an offshore setting, is presented in the following section.

No tests were completed with fresh water (zero water salinity). The DE values plotted for the zero water salinity values on these figures are the 'no dispersant applied' control test results for the oils. These control results are plotted to enable a rapid comparison of the untreated natural dispersion case to the dispersant applied tests over the range of salinities tested (5 to 30 ppt).

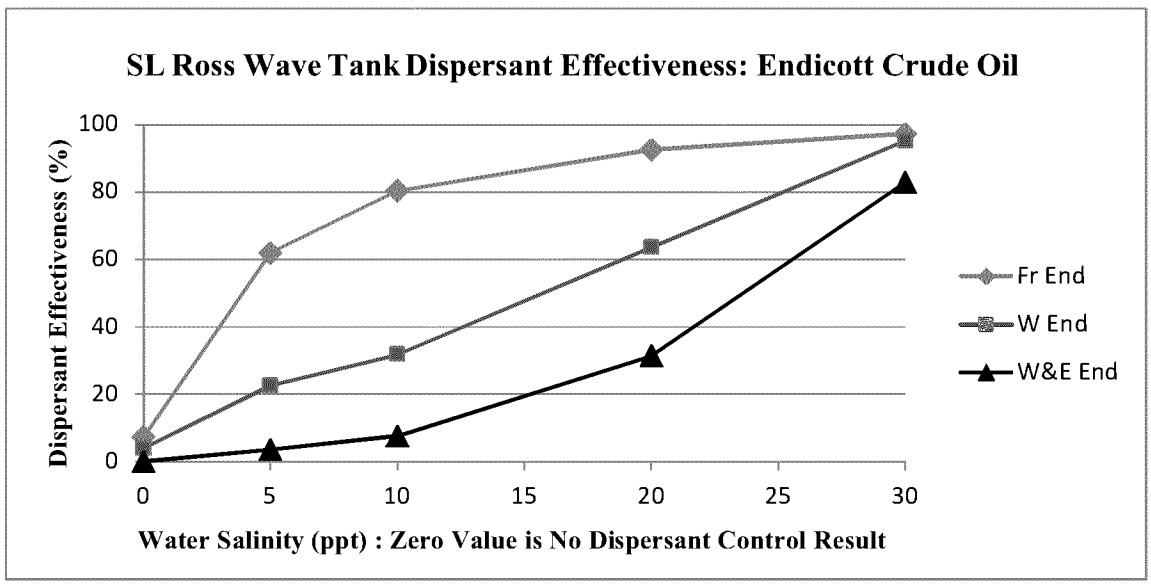

Figure 7-4 Dispersant Effectiveness versus Water Salinity: Endicott Crude Oil

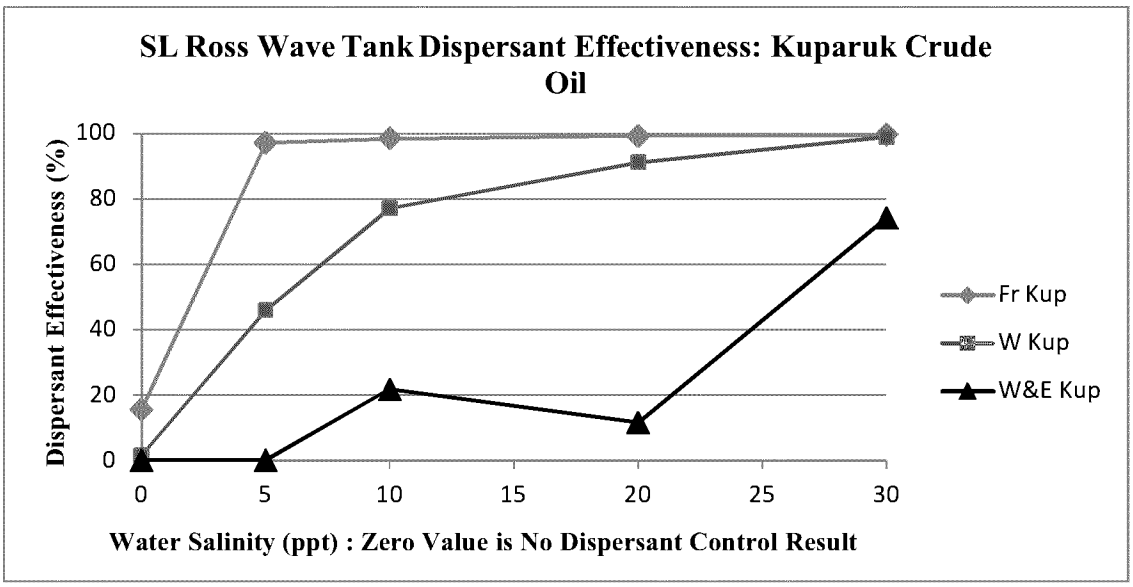

Figure 7-5 Dispersant Effectiveness versus Water Salinity: Kuparuk Crude Oil

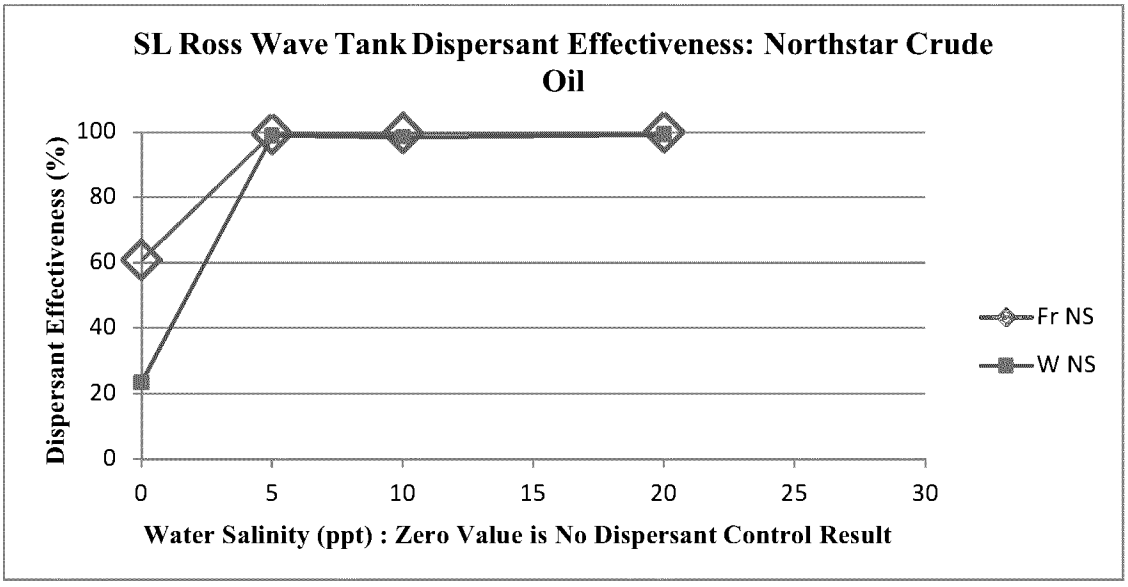

Figure 7-6 Dispersant Effectiveness versus Water Salinity: Northstar Crude Oil

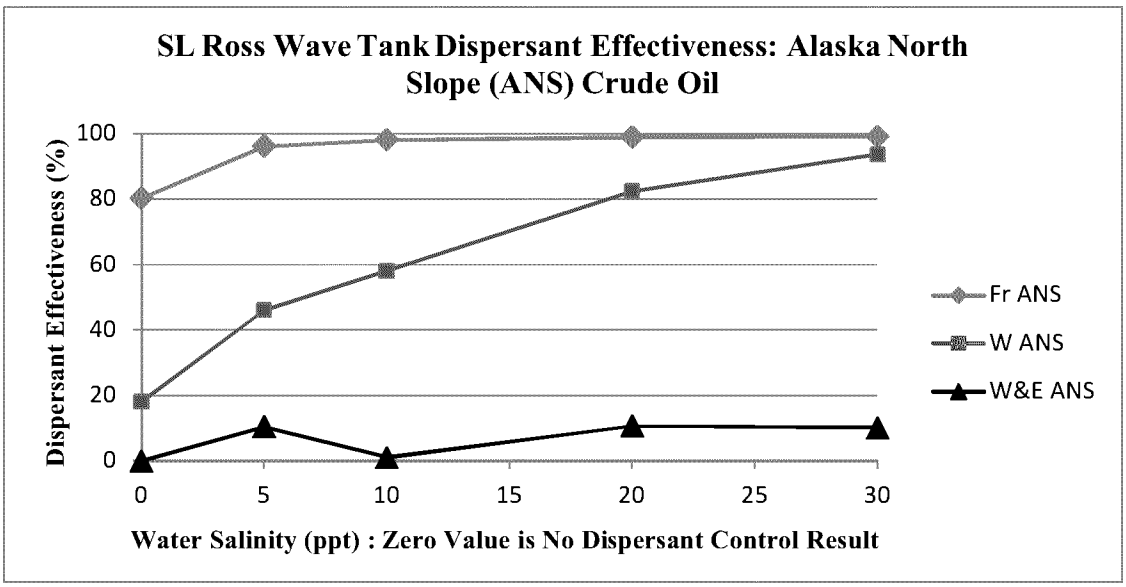

Figure 7-7 Dispersant Effectiveness versus Water Salinity: Alaska North Slope Crude Oil

The DE_{raw} values measured for the various oils tested showed consistent results. The fresh oils were more effectively dispersed than the weathered oils that were more effectively dispersed than the weathered and emulsified oils. The fresh and weathered Northstar crude oils were both completely dispersed at all water salinities (see Figure 7-6). With the exception of the Endicott crude oil, which has the highest fresh oil viscosity of those tested, the fresh oils registered high DE_{raw} (greater than 80%) at all water salinities tested. However, it is important to emphasize that the quality of the dispersions, as measured by the oil drop size distributions, generated varied over the range of water salinities tested and this issue is discussed in the next section. For three of the weathered oils the effectiveness of the dispersant increased as the water salinity increased. Significant dispersion (greater than 60%) of emulsified oil was achieved only for the highest water salinity (30 ppt) tests for the Endicott (Figure 7-4) and Kuparuk (Figure 7-5) oils. The emulsified ANS (Figure 7-7) did not disperse at any of the water salinities tested. Northstar crude did not form a stable water-in-oil emulsion.

About 80% of the fresh ANS (Figure 7-7) was lost to the water column in the control test (no dispersant applied); more than even the much lighter Northstar crude (Figure 7-6) where 60% was lost in the control test. The oil-water interfacial tension (o-w IFT) of the fresh ANS was measured to determine if the oil possibly contains production chemicals that might be affecting

the dispersion process. Chemicals are routinely added to crude oil streams during the production process and pipeline transportation to minimize emulsion formation, break water-in-oil emulsions and to improve the flow properties of the crude oil. The o-w IFT of the fresh ANS was measured to be approximately 13 dynes/cm^2. This is considerably lower than the o-w IFTs of the other Alaskan oils tested in this study which were 19.6 dynes/cm^2 for Kuparuk, 22.1 for Northstar and 27 for Endicott, and may explain the high natural dispersion of this oil when fresh. The less dense and much less viscous Northstar crude used in the testing has an o-w IFT of 22 dynes/cm^2. One would normally expect the less viscous Northstar crude oil to have a higher natural dispersion than the more viscous ANS but the natural dispersion for this oil was less than the ANS. This lower natural dispersion of the Northstar crude relative to the ANS can be attributed to Northstar's higher o-w IFT.

7.4.2 Dispersed Oil Drop Size Distributions

A LISST (Laser In-Situ Scattering and Transmissometry) device was deployed at 40 cm below the water surface during all of the tank tests. Figure 7-8 through Figure 7-15 show the results from these measurements. Two figures are provided for each of the test oils. All of the graphs show averaged data during elevated oil concentrations over the full test run. Only those data points where the oil concentration in the water column was 1.5 times the background oil concentration measured in the tank prior to the test are used in generating these averages. This ensures that only data during elevated oil concentrations are used in the analysis. The first figure in each set shows the average volume median diameter (VMD) of the oil drop size distributions. The second figure shows the average volume percent of the oil present in the water column in drops smaller than 70 microns in diameter. This value has been chosen because past research has shown that only oil in drops 70 microns and smaller are likely to be permanently dispersed in an ocean setting and those greater than 70 microns are likely to be temporarily entrained (Lunel, 1993). This study is the only comprehensive data set that we are aware of that documents the oil drop size distributions for chemically dispersed crude oils in an ocean setting.

The LISST device used in the testing can measure oil drops in the 5 to 500 micron range. Drops larger than this are not registered by the device. If a significant amount of oil is present in the

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water in drops larger than 500 microns then the oil drop distributions and oil concentrations measured by the LISST are not accurate. During each test the dispersed oil cloud was observed through the viewing window of the test tank and those tests where large oil drops were present (0.5 mm and larger) were identified. **Solid lines** and **enlarged data markers** in the following graphs denote where **reliable LISST data** was recorded, **dashed lines** indicate that the LISST data are **not reliable** due to the presence of large oil drops in the dispersion.

The dispersant effectiveness results presented in section 7.4.1 provide an indication of the percentage of oil removed from the water surface in the oil containment zone by breaking waves in the SL Ross dispersant effectiveness test tank. The results in this section provide additional information on the quality of the oil dispersions through the drop size distribution data. As discussed above it has been shown that drops greater than 70 mi6crons may only be temporarily entrained in certain ocean conditions so it is important to characterize the oil drop size distributions in the dispersions to determine how much of the dispersed oil is likely to remain dispersed. In Figure 7-8 and Figure 7-9 the oil drop size distributions for the fresh Endicott dispersions were reliable for all but the control (no dispersant applied) test. The oil VMD decreased linearly from about 190 microns at 5 ppt to about 110 microns at 30 ppt (Figure 7-8). The volume of drops with diameters less than 70 microns increased in a linear fashion from about 20 % at 5 ppt to 40 % at 30 ppt as seen in Figure 7-9. The LISST data for the weathered and weathered & emulsified tests with Endicott were valid only for the 30 ppt water tests. The trends in drop sizes from fresh to weathered to weathered & emulsified (W&E) oil are as would be expected. The fresh oil test had a smaller VMD and higher percentage of oil in drops less than 70 microns than were present in the weathered oil test and the weathered oil test had smaller drops and a higher percentage less than 70 microns than the W&E test. The oil drops in the Endicott fresh oil dispersion in 30 ppt salt water were the largest of the four fresh oils tested. How the drop size distributions reported in this section affect the estimates of ultimate dispersant effectiveness is presented in the following section 7.4.3.

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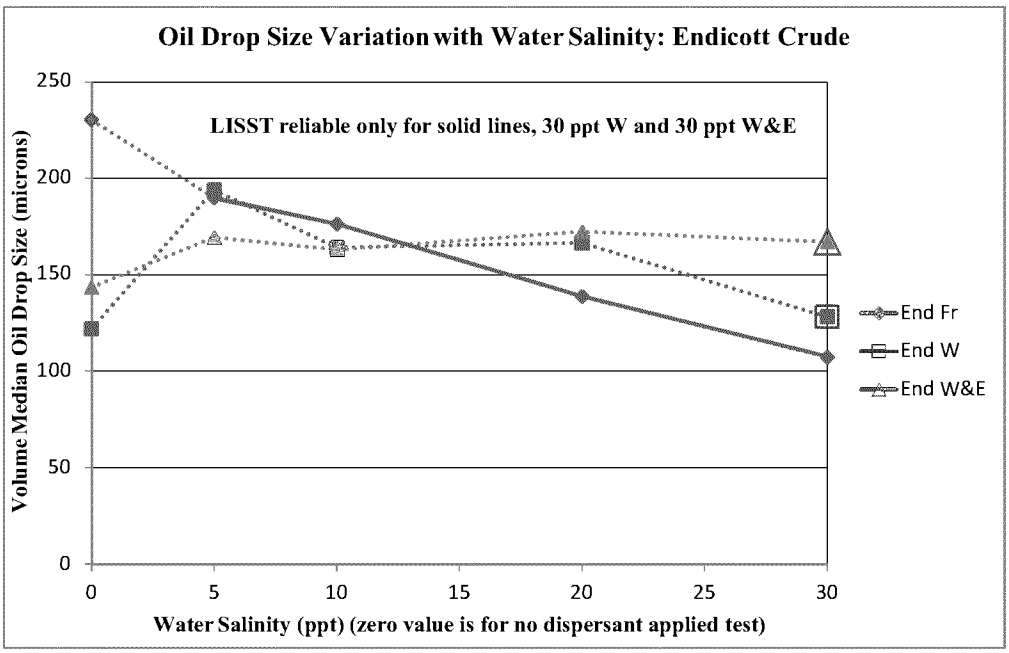

Figure 7-8 Oil Drop Size Variation Versus Water Salinity: Endicott Crude

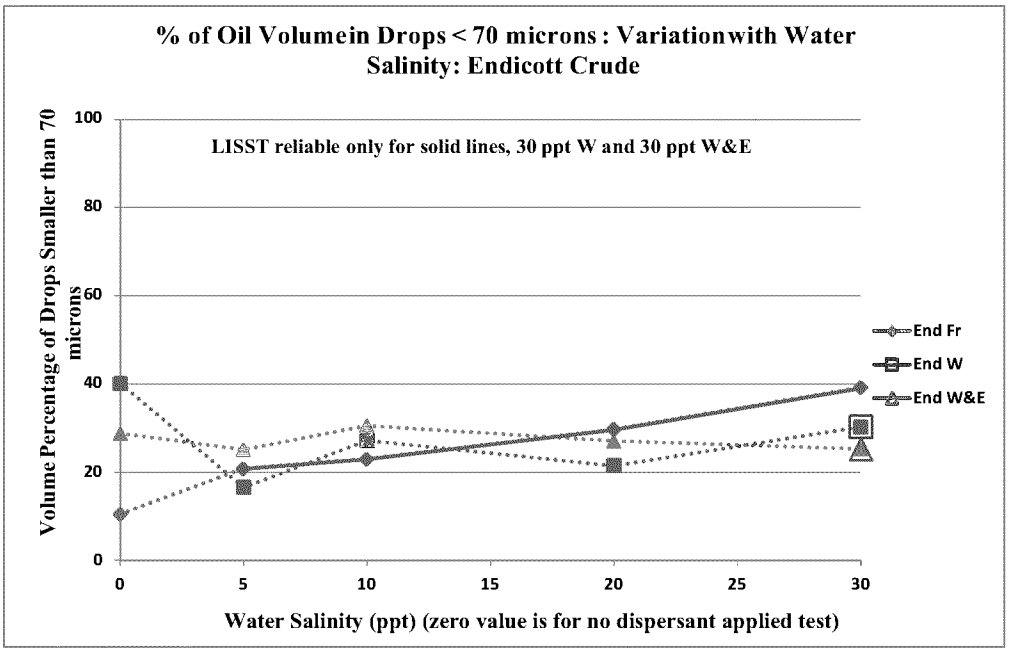

Figure 7-9 Volume Percent of Oil in Drops Less than 70 Microns: Endicott Crude

The LISST results for Kuparuk oil are summarized in Figure 7-10 and Figure 7-11. For both fresh and weathered Kuparuk crude the LISST data are reliable for both the 20 and 30 ppt water salinity tests. The oil drop VMDs for both the fresh and weathered Kuparuk were smaller than 70 microns for the 30 ppt salinity water as seen in Figure 7-10 and a high percentage of oil was

present in oil drops less than 70 microns in both cases (85% for the fresh oil and 68% for weathered oil, as seen in Figure 7-11). The VMD oil drop sizes were about 125 microns for both the fresh and weathered oil in the 20 ppt salinity water tests, considerably larger than in the 30 ppt tests (Figure 7-10). The W&E dispersion in 30 ppt salt water had a VMD of about 180 microns, and only about 25% of the dispersed oil was in drops less than 70 microns.

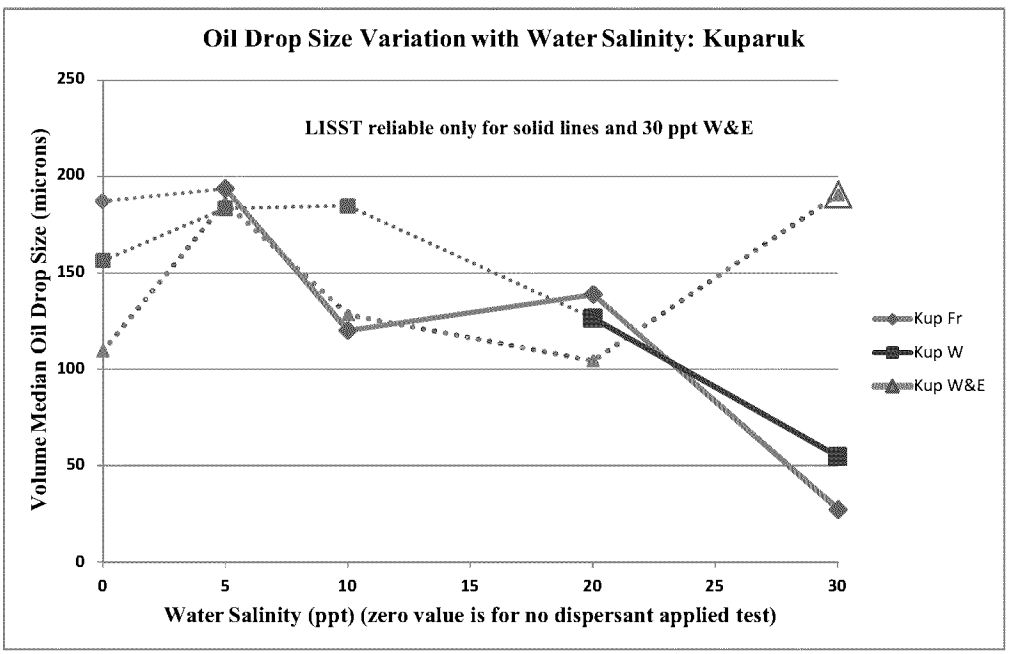

Figure 7-10 Oil Drop Size Variation Versus Water Salinity: Kuparuk Crude

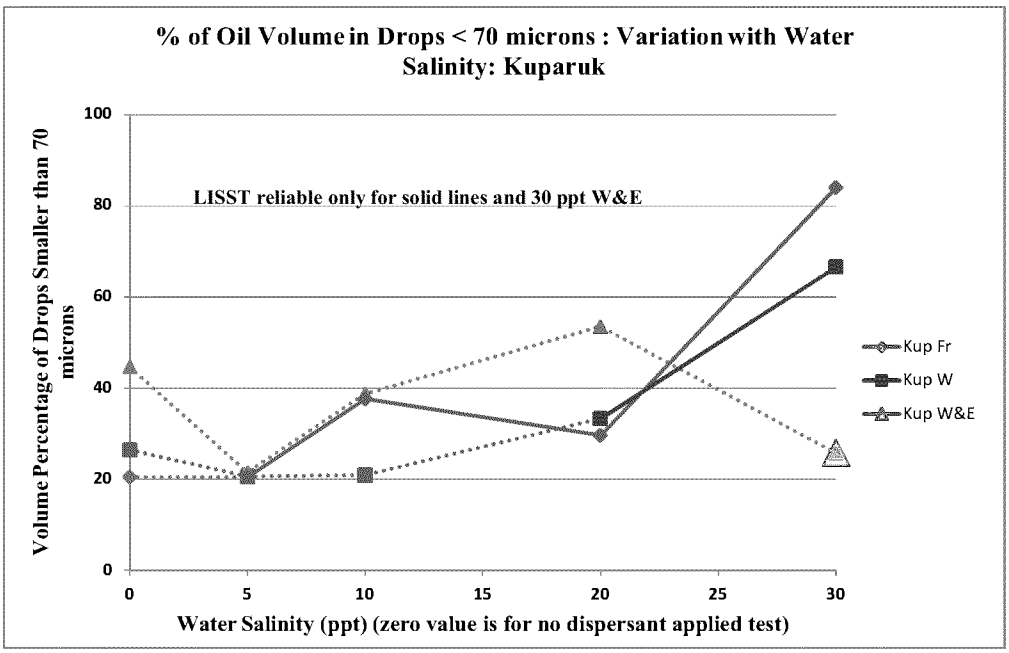

Figure 7-11 Volume Percent of Oil in Drops Less than 70 Microns: Kuparuk Crude

The LISST results for Northstar oil are summarized in Figure 7-12 and Figure 7-13. For Northstar crude the LISST data was reliable for all but the no dispersant applied control case. Tests were not conducted with Northstar crude oil at 30 ppt water salinity because the dispersant was 100% effective in dispersing the oil at 20 ppt and the dispersion generated in the 20 ppt water was a coffee colored dispersion which indicates a dispersion with a small oil drop size distribution. The oil drop VMDs for both the fresh and weathered Northstar were 70 microns or smaller for the 20 ppt salinity water as seen in Figure 7-12. About 95% of oil was present in oil drops less than 70 microns for the fresh oil and about 58% for weathered oil, as seen in Figure 7-13. The VMD oil drop sizes for the fresh oil test at 5 ppt and the weathered oil tests at 5 and 10 ppt were considerably larger (ranged between 150 and 180 microns as seen in Figure 7-12).

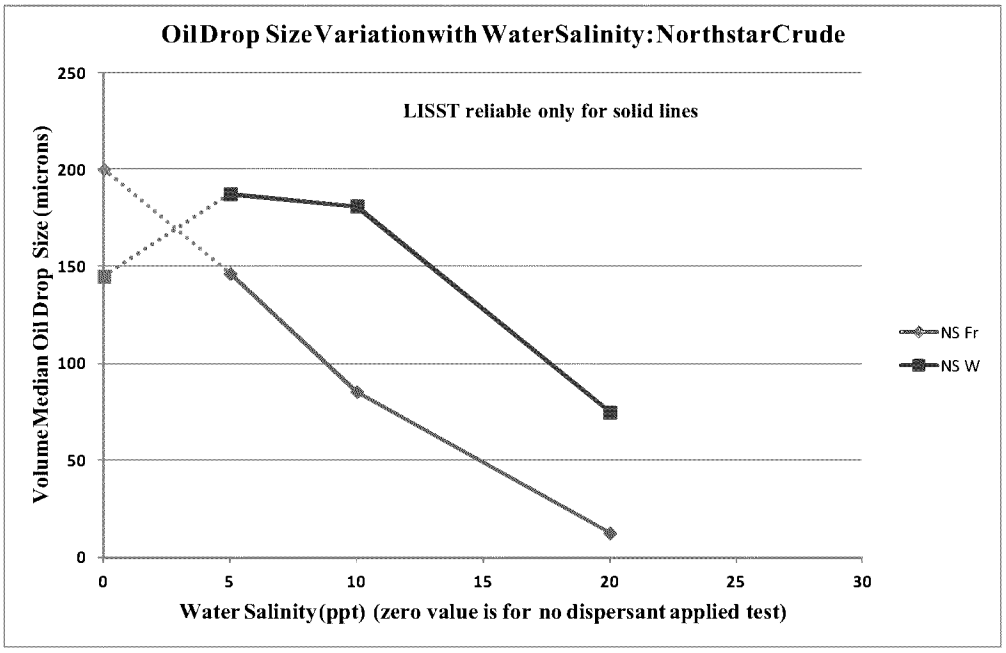

Figure 7-12 Oil Drop Size Variation Versus Water Salinity: Northstar Crude

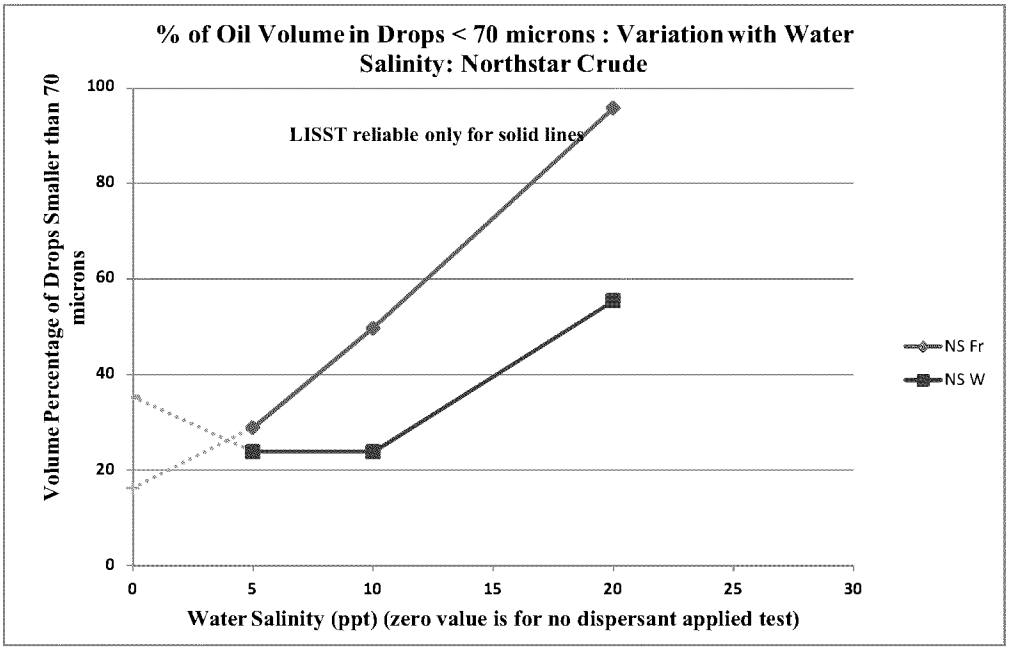

Figure 7-13 Volume Percent of Oil in Drops Less than 70 Microns: Northstar Crude

The LISST results for ANS oil are summarized in Figure 7-14 and Figure 7-15. For ANS crude the LISST data was reliable for the fresh oil tests at all salinities and at both the 20 and 30 ppt water salinity for the weathered oil. The LISST data was not reliable for any of the control tests (no dispersant applied) or for any of the W&E tests. The oil drop VMDs for the fresh oil were

about 25 microns and for the weathered ANS were about 125 microns for the 30 ppt salinity water as seen in Figure 7-14. About 90% of the oil was present in oil drops less than 70 microns for the fresh ANS test at 30 ppt but only 30 % for the weathered oil test (see Figure 7-15). In the 20 ppt salinity water tests the VMD oil drop sizes were about 60 microns in the fresh oil test and 160 microns with the weathered oil (Figure 7-14). In the 10 ppt water salinity tests for ANS the oil drop VMD increased to about 160 microns, similar to the weathered oil value at 20 ppt. The oil drop VMD increased to nearly 200 microns in the 5 ppt water salinity test.

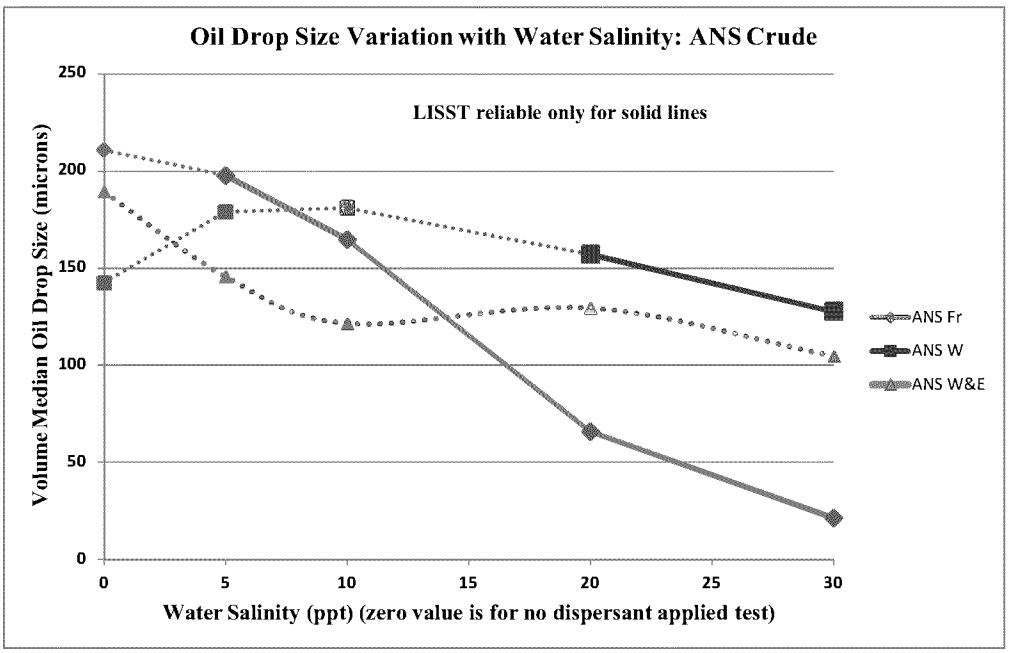

Figure 7-14 Oil Drop Size Variation Versus Water Salinity: ANS Crude

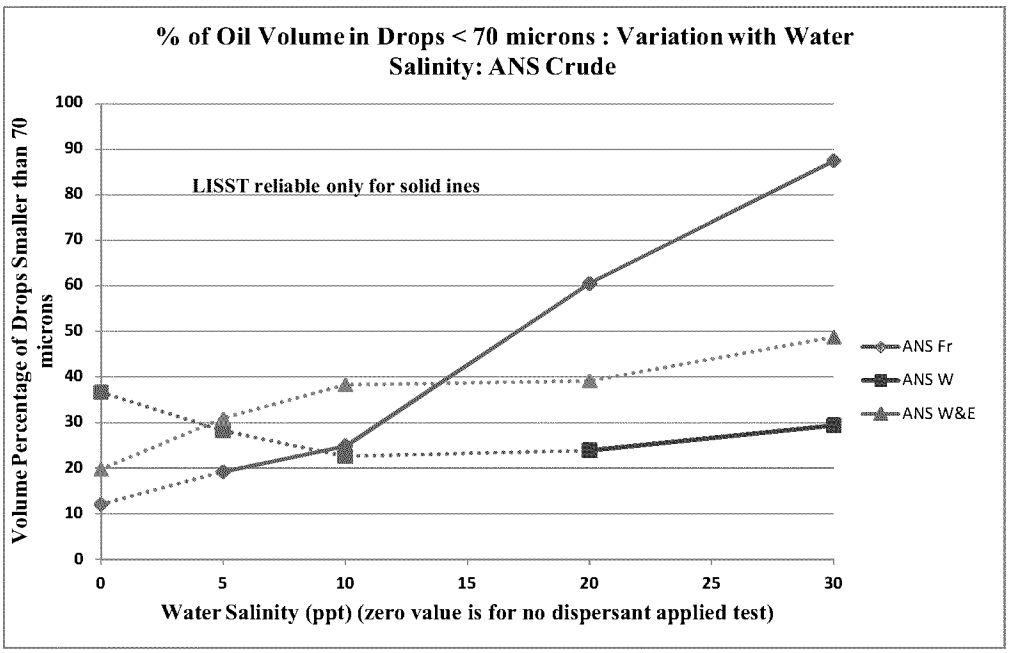

Figure 7-15 Volume Percent of Oil in Drops Less than 70 Microns: ANS Crude

7.4.3 Drop Size Adjusted Dispersant Effectiveness Estimates

The raw dispersant effectiveness (DE_{raw}) estimates presented in section 7.4.1 have been adjusted by multiplying the DE_{raw} values by the volume fraction of oil present in drops smaller than 70 microns. The 70 micron drop size value has been reported as being the maximum oil drop size that will remain dispersed based on field tests that utilized 7 different pre-mixed oil and dispersant combinations and wind conditions varying from 1.5 m/s to 7 m/s (Lunel, 1993). A second set of adjusted dispersant effectiveness results has been prepared using a 125 micron oil diameter cutoff to demonstrate the sensitivity of the estimate to the cutoff drop diameter. The 125 micron cutoff has been used based on additional accounts that have indicated that oil drops larger than 70 microns (100 microns) can remain dispersed (Neff 1990, Forrester 1971). It is possible that in heavier seas larger oil drops would be dispersed for long enough periods that even if they re-surfaced they would form sheens and not reform into thick slicks. The drop size data used to generate these adjusted DE values are strictly reliable only for the solid line and large open symbol data shown on these figures due to the upper limit of drop size detectability of the LISST device used to measure the drops, as was previously discussed. For those cases where the LISST data are not reliable (dashed lines) the adjusted DE estimates are likely higher than the

actual adjusted effectiveness would be because the LISST is not registering the presence of large oils drops which would result in a lower volume fraction of the oil being present in the small drop size categories.

The un-adjusted or raw DE graphs presented in 7.4.1 are duplicated in this section and shown on the same page as the adjusted DE graphs for easy comparison of the results. The 70 micron adjusted dispersant effectiveness (DE_{70}) values are generally lower than the raw DE values. The lower water salinity tests also generally had a greater reduction in DE when compared to the 30 ppt tests. Since many of the low salinity tests also had drop sizes outside of the range of the LISST device the adjusted DE values reported are also likely exaggerated. This would indicate that significantly larger oil drops than 70 microns are being removed from the containment zone in the SL Ross wave tank and that larger oil drops were generally formed as the water salinity decreased. When the oil drop size diameter cutoff for successful dispersion is relaxed to 125 microns the DE_{125} estimates generally increase by about 15 to 20% across all oils and water salinities but there was still a significant reduction in dispersant effectiveness compared to the unadjusted values.

The Endicott crude was the most difficult to disperse of the 4 oils. The adjusted DE_{70} of the fresh and weathered Endicott were only 40 and 30 %, respectively (see Figure 7-17). For the fresh Endicott there was a linear reduction in DE_{70} as the water salinity decreased. The DE_{70} in 5 ppt salt water was 18%.

For the Kuparuk crude the fresh and weathered DE_{70} values were about 85% and 65%, respectively (see Figure 7-20). The reduction in DE_{70} as the salinity decreased was again linear if the 20 ppt fresh oil value is treated as an outlier. The rate of decrease in effectiveness for Kuparuk was higher than for the Endicott. The DE_{70} in 5 ppt salt water was 20ppt, similar to the Endicott value. The weathered Kuparuk DE_{70} is slightly less than the fresh DE_{70} and reduced with declining salinity at a similar or slightly higher rate.

For the Northstar crude oil, the lightest product tested, the fresh oil DE_{70} at 20 ppt (the highest water salinity tested with this oil) was about 95%. The DE_{70} again dropped linearly, as the

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salinity decreased, to a value of about 30% in 5 ppt salt water (see Figure 7-23). The weathered Northstar DE_{70} was about 75% in 20 ppt water and dropped to 40% in both 10 and 5 ppt salt water.

The ANS DE_{70} for fresh oil in 30 ppt salt water was over 90% and again decreased linearly to about 20% in 5 ppt water (see Figure 7-26). The weathered ANS DE_{70} was only 50% in 30 ppt salt water and dropped to below 30% in 20 ppt water.

The highest DE_{70} recorded for any of the emulsified oils was 20% in 30 ppt salt water.

When the oil drop size diameter cutoff for successful dispersion is relaxed to 125 microns the DE_{125} estimates generally increase by about 15 to 20% across all oils and water salinities when compared to the DE_{70} values. This is strictly a result of an additional 15 to 20% of the oil in the dispersion being present in drops with sizes between 70 and 125 microns.

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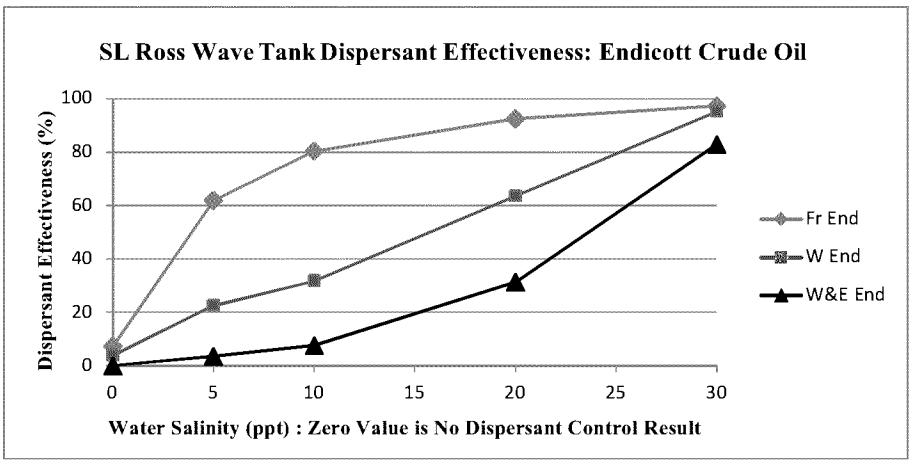

Figure 7-16 Dispersant Effectiveness versus Water Salinity: Endicott Crude Oil (copy of Figure 7-4)

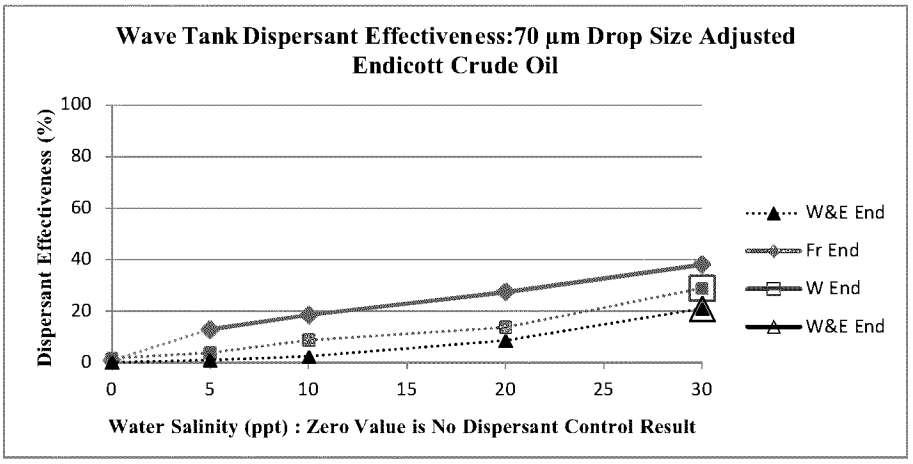

Figure 7-17 Drop Size Adjusted (70µm) Dispersant Effectiveness versus Water Salinity: Endicott Crude Oil

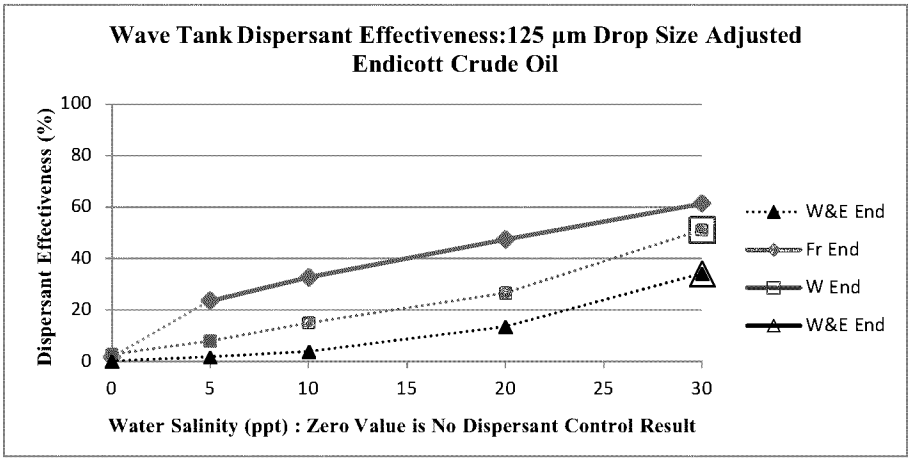

Figure 7-18 Drop Size Adjusted (125µm) Dispersant Effectiveness versus Water Salinity: Endicott Crude Oil

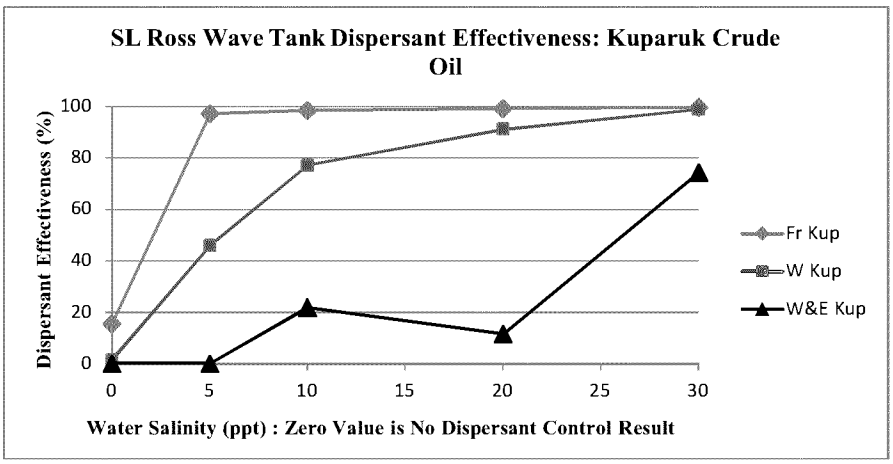

Figure 7-19 Dispersant Effectiveness versus Water Salinity: Kuparuk Crude Oil (copy of Figure 7-5)

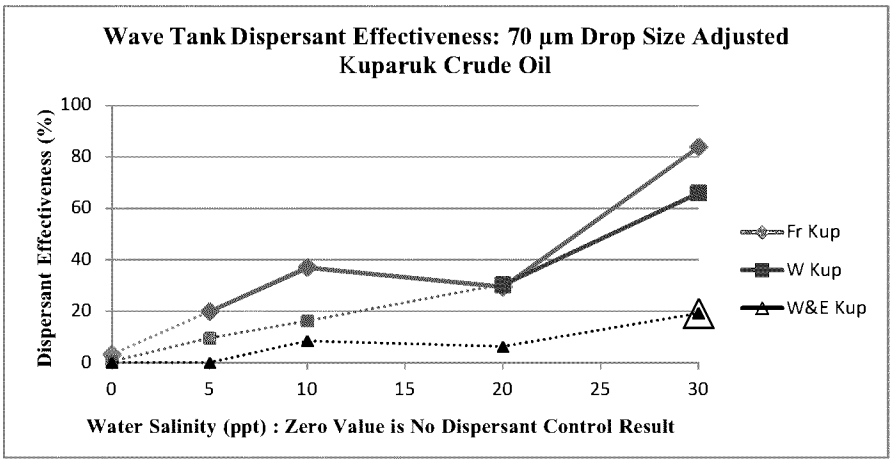

Figure 7-20 Drop Size Adjusted (70µm) Dispersant Effectiveness versus Water Salinity: Kuparuk Crude Oil

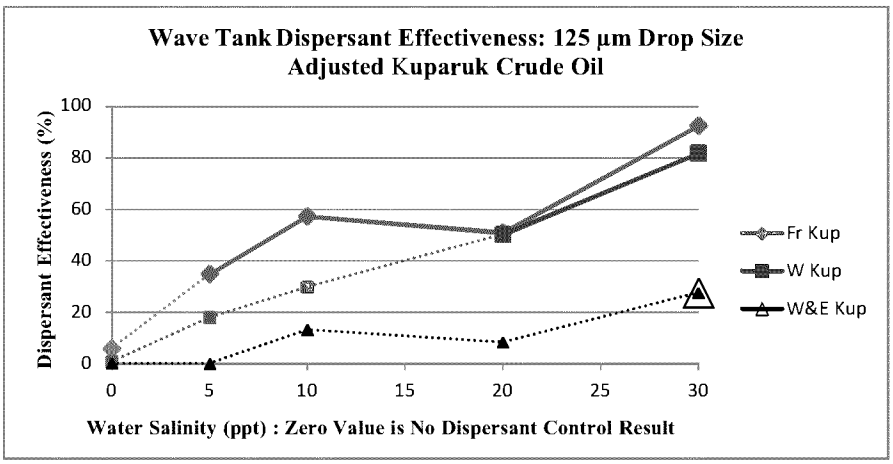

Figure 7-21 Drop Size Adjusted (125µm) Dispersant Effectiveness versus Water Salinity: Kuparuk Crude Oil

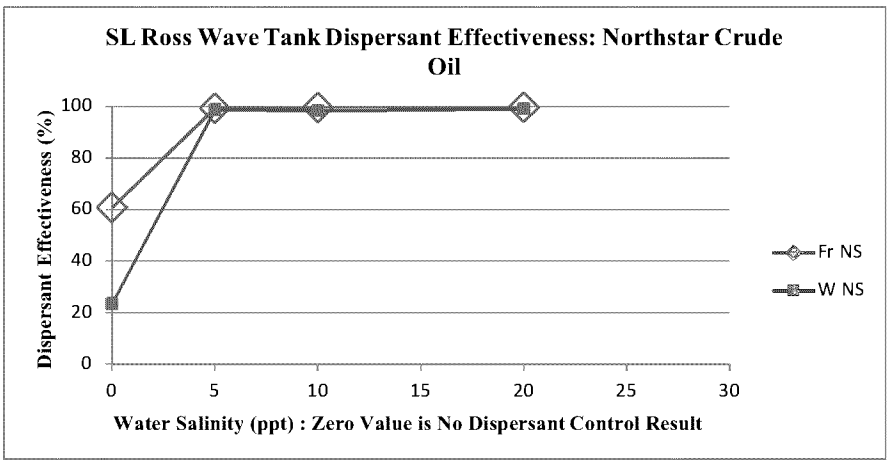

Figure 7-22 Dispersant Effectiveness versus Water Salinity: Northstar Crude Oil (copy of Figure 7-6)

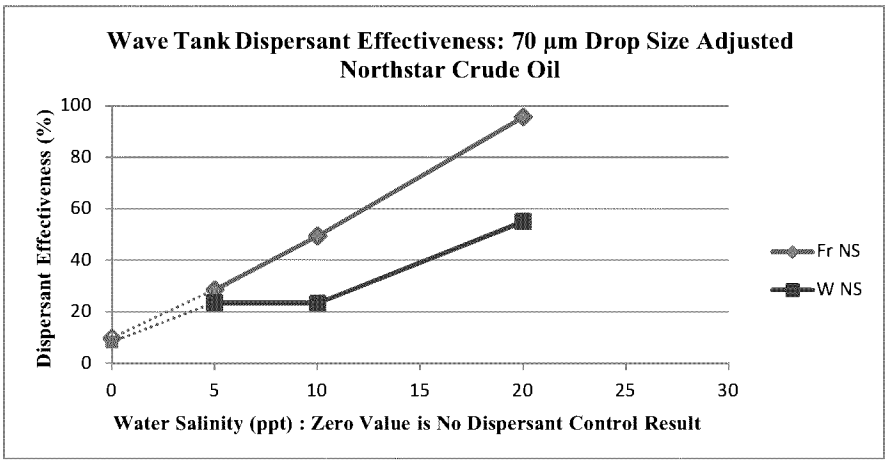

Figure 7-23 Drop Size Adjusted (70µm) Dispersant Effectiveness versus Water Salinity: Northstar Crude Oil

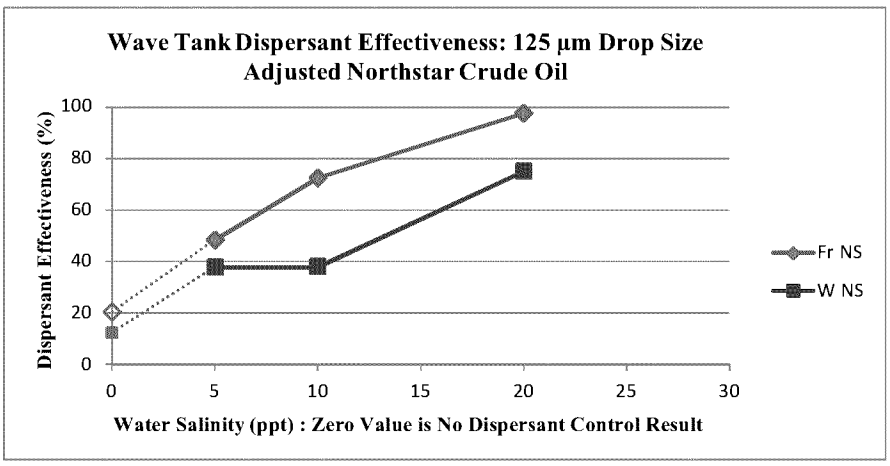

Figure 7-24 Drop Size Adjusted (125µm) Dispersant Effectiveness versus Water Salinity: Northstar Crude Oil

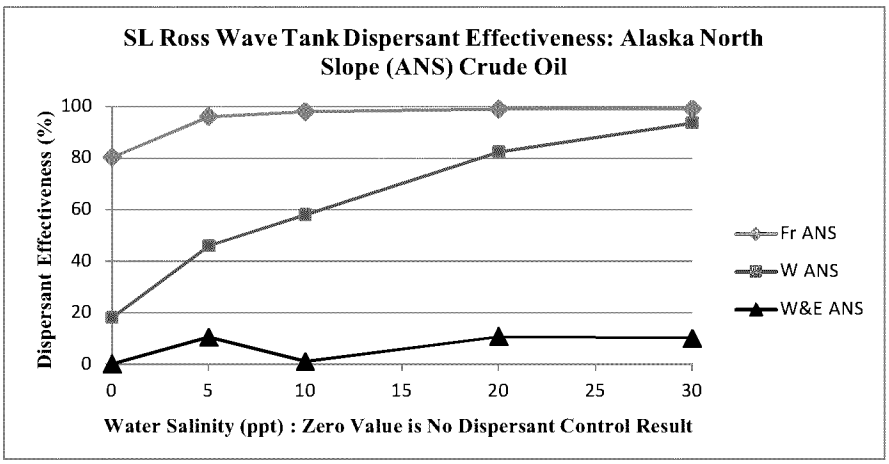

Figure 7-25 Dispersant Effectiveness versus Water Salinity: ANS Crude Oil (copy of Figure 7-7)

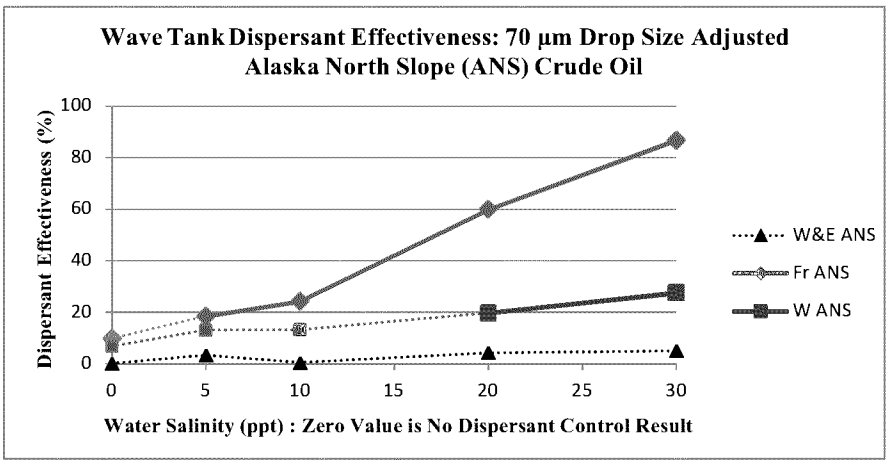

Figure 7-26 Drop Size Adjusted (70µm) Dispersant Effectiveness versus Water Salinity: ANS Crude Oil

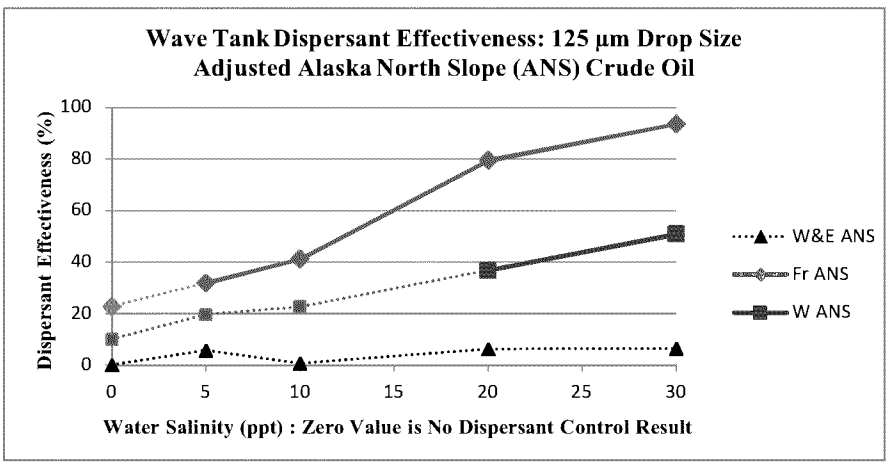

Figure 7-27 Drop Size Adjusted (125µm) Dispersant Effectiveness versus Water Salinity: ANS Crude Oil

7.4.4 SL Ross Tank Test Results Discussion

The dispersant had an effect on all of the oils at all water salinities (5 through 30 ppt) when compared to the no dispersant applied control case. The oil drops sizes in the dispersions increased as the salinity decreased demonstrating the reduced effect of the Corexit 9500 dispersant on the oils at lower water salinities.

Final dispersant effectiveness estimates (DE_{70}) were made by adjusting the quantity removed from the surface by the volume percent of oil present in drops less than 70 microns.

The most complete data sets collected (due to limitations of the LISST in measuring large oil drops) were for the fresh oil tests. The results for the fresh oils indicate that the DE_{70} values are highest for the 30 ppt water and in all cases drop linearly as the test water salinity decreased to 5 ppt. The Northstar crude was most easily dispersed with complete dispersion (> 95% DE_{70} in 20 ppt salt water), followed by fresh ANS (95% DE_{70}), fresh Kuparuk (85% DE_{70}) and Endicott (40% DE_{70}). The DE_{70} dropped linearly to between 15 to 25 % for the oils tested as the water salinity decreased to 5 ppt.

An alternate DE_{125} was also estimated using a 125 micron cutoff to demonstrate the sensitivity of the drop size cutoff for permanent dispersion on the final DE estimate. The 125 micron value was arbitrarily chosen as a significantly larger drop diameter to investigate the effect on the estimated DE. The DE_{125} estimates generally increase only by about 15 to 20% across all oils and water salinities when compared to the DE_{70} values. The same trends in DE with water salinity and oil type are present in the DE_{125} results.

The oil drops in some of the tests were visibly larger than the upper measurement limit of the LISST device and reliable drop size data could not be gathered for these tests. Development of an in-situ oil drop measurement system capable of cost-effectively measuring drop sizes in the 10 to 3000 micron range would improve the state-of-the art in oil dispersion monitoring both in large tank and field test conditions.

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The SL Ross wind wave tank was outfitted with a new computer controlled paddle and wave dampening beaches in 2013. This upgrade now permits the creation of breaking waves at a specific location and with a specific frequency and wave height. In the tank's previous configuration the wave generation was limited to a confused sea type of motion with no significant plunging wave activity. Dispersant effectiveness test results in the old wind-wave facility have correlated well with results collected in the Ohmsett wave tank (SL Ross 2003). This is the first extensive series of tests conducted in the new facility with the use of the plunging or breaking waves that have been described in Section 7.2. There was no visible loss of oil from the containment zone at the surface of the tank during the tests. The breaking waves did propel significant quantities of small and large oil drops into the upper 2/3 of the water depth when the oil was fresh and relatively non-viscous. In tests conducted with the old tank configuration large oil drops were not driven as deep into the water column and then re-surfaced more quickly than in the breaking wave environment. This provided less time for the sub-surface movement of the larger oil drops out of the containment zone. This is the likely reason for the high unadjusted dispersant effectiveness results in the tests where the oil drop sizes were significantly greater than 70 microns. Due to the presence of multiple beach elements in the tank it is not possible to collect oil surfacing outside of the bubble containment zone. Based on the experience gained in this test program we recommend that smaller breaking waves be used in future tests to minimize the depth of penetration of oil in each breaking event and minimize the loss of large dispersed oil drops from the containment region.

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9 Appendix A : Detailed Dispersant Effectiveness Tables

Table 9-1 Percentage of Time Dispersants Would Be Effective at Wind Station 2 (Chukchi Sea Offshore Wainwright)

Percent of Time Dispersants Effective (48 hour Calm Wind Grace Period)						
	31 year Data Analysis (1979 to 2009)			10 year Data Analysis (2000 to 2009)		
Month	Favorable	Impaired	Not Favorable	Favorable	Impaired	Not Favorable
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
6	77	2	21	77	2	21
7	83	2	15	83	2	15
8	90	2	7	87	3	10
9	89	6	5	90	5	4
10	86	9	5	88	9	3
11	80	9	11	82	9	9
12	0	0	0	0	0	0

Table 9-2 Percentage of Time Dispersants Would Be Effective at Wind Station 3 (Beaufort Sea Offshore Barrow)

Percent of Time Dispersants Effective (48 hour Calm Wind Grace Period)						
	31 year Data Analysis (1979 to 2009)			10 year Data Analysis (2000 to 2009)		
Month	Favorable	Impaired	Not Favorable	Favorable	Impaired	Not Favorable
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
6	0	0	0	0	0	0
7	73	2	25	76	2	22
8	82	2	15	79	3	19
9	87	3	10	87	4	9
10	81	5	14	86	6	8
11	0	0	0	0	0	0
12	0	0	0	0	0	0

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Table 9-3 Percentage of Time Dispersants Would Be Effective at Wind Station 4 (Beaufort Sea Offshore Prudhoe Bay)

Percent of Time Dispersants Effective (48 hour Calm Wind Grace Period)						
	31 year Data Analysis (1979 to 2009)			10 year Data Analysis (2000 to 2009)		
Month	Favorable	Impaired	Not Favorable	Favorable	Impaired	Not Favorable
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
6	0	0	0	0	0	0
7	69	3	28	71	3	26
8	79	3	18	75	3	22
9	86	5	10	87	4	10
10	80	7	13	84	7	9
11	0	0	0	0	0	0
12	0	0	0	0	0	0

Table 9-4 Percentage of Time Dispersants Would Be Effective at Wind Station 4 (Beaufort Sea Offshore East of Barter Island)

Percent of Time Dispersants Effective (48 hour Calm Wind Grace Period)						
	31 year Data Analysis (1979 to 2009)			10 year Data Analysis (2000 to 2009)		
Month	Favorable	Impaired	Not Favorable	Favorable	Impaired	Not Favorable
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
6	0	0	0	0	0	0
7	80	2	17	81	2	17
8	82	4	14	78	4	17
9	87	4	9	87	4	10
10	82	6	13	79	6	15
11	0	0	0	0	0	0
12	0	0	0	0	0	0

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10 Appendix B : Annotated Bibliography: Past Research Relevant to Dispersion of Alaskan Oils in the US Beaufort and Chukchi Seas

Abbasova, A. et al. 2005. Evaluation of dispersants for use in the Azerbaijan region of the Caspian Sea.
Oil Type: Chirag crude oil (Caspian Sea)
Dispersant Type: Finasol OSR51, Superdispersant 25, Corexit EC 9527a, Corexit EC 9500a, Slickgone NS, Inipol IP90
Water Temperature: assumed to be EPA standard temp of 23 ± 3 °C
Water Salinity: 12 ppt (Caspian Sea Water) Six dispersants were tested on Chirag crude oil in 12 ppt water. All dispersants were effective in dispersing this crude oil at this low salinity. Average effectiveness values ranged from 72 to 84%.
Presence of Ice: Not studied.
Energy Level: EPA Baffled Flask.

Anderson, J.W., D.L. McQuerry, S.L. Kiesser. 1985. Laboratory evaluation of chemical dispersants for use on oil spills at sea
Oil Type: Alaska North Slope crude
Dispersant Type: 14 different dispersants. Dose set to achieve 90 % dispersion of ANS in MNS apparatus. Primary purpose to investigate toxicity of chemically dispersed oil.
Water Temperature: 15 °C.
Water Salinity: 30 ppt
Presence of Ice: Not studied.
Energy Level: MNS standard mixing (1.0 inch of water pressure)

Belore, R., S. Ross. 2000. Laboratory study to compare the effectiveness of chemical dispersants when applied dilute versus neat
Oil Type: Alaska North Slope crude
Dispersant Type: Corexit 9500 and Corexit 9527. Dispersant was applied neat and diluted with salt water. Corexit 9527 performed as well when diluted as when applied neat. Corexit 9500's performance was reduced when applied diluted with sea water. Application of Corexit 9500 in a neat form was recommended.
Water Temperature: 17 °C
Water Salinity: 32 ppt
Presence of Ice: Not studied
Energy Level: SL Ross wave tank, energy not varied.

Belore, R. 2003. Large wave tank dispersant effectiveness testing in cold water
Oil Type: fresh and weathered Alaska North Slope and Hibernia crude
Dispersant Type: Corexit 9500 and Corexit 9527.
Water Temperature: -0.5 to 2.4 °C. Both oils were readily dispersed by both dispersants at the cold test temperatures.
Water Salinity: 32 ppt
Presence of Ice: Not studied
Energy Level: Ohmsett breaking wave conditions. The average wave amplitude for the tests ranged between 16.5 and 22.5 cm and the average wave period was between 1.7 and 1.9 seconds.

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Blondina, G., M Singer, I. Lee, M. Ouano, M. Hodgins, R. Tjeerdema. 1999. Influence of Salinity on Petroleum Accommodation by Dispersants.
Oil Type: various including Prudhoe Bay crude
Dispersant Type: Corexit 9500 and Corexit 9527
Water Temperature: 15 °C
Water Salinity: 0 to 35 ppt. For Prudhoe Bay crude oil 9500 was equally effective from 20 to 35 ppt and effectiveness dropped off below 20 ppt. 9527 effectiveness dropped off below 30 ppt.
Presence of Ice: Not studied
Energy Level: modified Swirling Flask test.

Brandvik, P.J., 0.0. Knudsen, M.O. Moldestad and P.S. Dating, 1995. Laboratory Testing of Dispersants Under Arctic Conditions
Oil Type: Norwegian Crude Oils
Dispersant Type: Corexit 9500 & 9527 plus 12 others, 5 main dispersants tested were Inipol IPF, Inipol IPC, Enersperse 700, Finasol OSR-52 and Dasic Fresh Water.
Water Temperature: 0°C
Water Salinity: 5 to 35 ppt. Dispersants formulated for low salinity performed well at low salinities but not at high salinities. Traditional dispersants formulated for high salinity water did not perform well at low salinities. Many dispersants performed well at the low test temperature on most of the oils tested but effectiveness was a function of the oil type.
Presence of Ice: Not studied
Energy Level: IFP test, energy not varied

Brown, H.M., R.H. Goodman. 1985. Dispersant Effectiveness in Cold Water
Oil Type: Federated crude (Alberta Sweet Mixed Blend)
Dispersant Type: Corexit 9527, and CRX-8.
Water Temperature: -2 °C.
Water Salinity: Tests were conducted at 28 ppt water salinity
Presence of Ice: Slush ice present in test #6 only
Energy Level: Low energy non-breaking waves were used. In 20 cm waves 24 to 33% of the spilled oil was dispersed in the water column even 20 hours after the wave basin energy had been stopped. The single test conducted with slush ice resulted in more oil dispersion than in open water. This was attributed to the shear imparted by the moving slush ice

Brown, H.M., R.H. Goodman. 1987. Outdoor Wave Tank Tests
Oil Type: Alaska North Slope Crude (ANS) weathered 12 to 24 hours on tank prior to dispersant application.
Dispersant Type: Corexit 9527, 9550 and Enersperse 700 were tested. Enersperse was least effective 38% and Corexit 9527 and 9550 were similar with 53 to 63% effectiveness at higher wave energy.
Water Temperature: Water temperature was not varied but tests were conducted at 0 to 5 °C.
Water Salinity: Tests were conducted at 32 ppt water salinity
Presence of Ice: Not studied
Energy Level: The single test conducted with lower wave energy had 19% less effectiveness than the higher energy test (42% versus 61%).

Brown, H.M., D.K.Weiss, R.H. Goodman. 1990. Emulsion formation in dispersant-treated crude oil.
Oil Type: Alaska North Slope and Drift River crude
Dispersant Type: Corexit 9500 and Corexit 9527. For the non-dispersed portions of slicks of Drift River crude, the application of dispersants enhanced the rate of water incorporation and also increased the viscosity, while the opposite effect was observed for North Slope crude oil: the treated slicks did not emulsify as fast or achieve as high viscosities.
Water Temperature: -not reported
Water Salinity: 30 ppt
Presence of Ice: Not studied
Energy Level: Esso wave basin. The average wave amplitude for the tests was 20 cm and the average wave period was between 1.6 seconds.

Brown and Goodman 1996. The Use of Dispersants in Broken Ice
Oil Type: Federated crude oil
Dispersant Type: Corexit 9527, 9500
Water Temperature: -1.2 °C
Water Salinity: Tests were conducted at 30 ppt water salinity
Presence of Ice: Condition 1: Five-metre diameter booms were positioned and frozen into the ice. Before oil was spilled into the boomed area, low amplitude waves were generated to break the ice. Several such experiments were conducted involving different ice thicknesses and ice coverages. In all cases oil was effectively dispersed (>90% dispersion) even in 95% ice cover and low wave levels
Condition 2: Ice slot was cut into fully formed ice sheet. Oil was placed in the slot. No measureable natural dispersion occurred under low energy with no ice present. With slush ice present some natural dispersion occurred. When dispersant was added to oil in slush ice almost all oil dispersed
Energy Level: Low energy swells by wave board in ESSO outdoor wave basin.

Byford, D., P. Green, A. Lewis. 1983. Factors Influencing the Performance and Selection of Low-Temperature Dispersants.
Oil Type: Lago Medio, North Slope Crude, Medium Fuel Oil
Dispersant Type: Corexit 9527, Corexit 9550 BP1100WD, Fiansol OSR5, Dispolene 34S, Arcochem D609
Water Temperature: 0 and 10 °C. In all cases the dispersant performance was not reduced in the lower temperatures and in some cases was enhanced.
Water Salinity: 0 to 33 ppt. Water salinity was found to affect dispersant performance to varying degrees. One product worked equally as well at all salinities but was a poor performer compared to other products. Product names were not attached to results.
Presence of Ice: 100% broken ice pieces (5 mm x10mmx10mm) in BP wave tank tests. Results suggest that dispersant performance can be enhanced due to the enhanced mixing caused by the pumping action between ice pieces. Dispersion was at least as good in ice conditions as in open water in all tests.
Energy Level: standard WSL test and BP wave tank with 40 mm wave amplitude

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Chandrasekar, S. G.A., Sorial, J.W. Weaver. 2003. Determining dispersant effectiveness data for a suite of environmental conditions.
Oil Type: Prudhoe Bay (PBC), South Louisiana (SLC) crude and #2 Fuel oil. Slight reduction in effectiveness was identified with weathered (10 to 20% loss) versus fresh oil. For PBC the reduction was less than 5%.
Dispersant Type: Corexit 9500 and Dispersit-SPC 1000
Water Temperature: 5, 22 and 35 °C. Increased dispersion with increased temperature for SLC, maximum dispersion at 22°C for both PBC and #2 Fuel oil.
Water Salinity: standard BF 34 ppt assumed
Presence of Ice: Not studied
Energy Level: 150, 200 and 250 rpm on shaker table. Higher effectiveness at higher energies in all tests.

Chandrasekar, S.; Sorial, G.A.; Weaver, J.W. 2006. Dispersant effectiveness on oil spills – impact of salinity.
Oil Type: Alaskan Prudhoe Bay (PBC) fresh, 10% and 20% evaporated, South Louisiana crude oil (SLC) fresh, 10% and 20% evaporated, No. 2 Fuel Oil (2FO) fresh, 3.8% and 7.6% evaporated. Weathered PBC dispersed as well as fresh at 200 rpm and over the full range of temperatures.
Dispersant Type: Dispersants identified as A & B only
Water Temperature: 5, 22 and 35 °C. Highest effectiveness at 250 rpm for the most weathered PBC was achieved at 22 °C.
Water Salinity: 10, 20, 34 ppt. Salinity did not significantly (less than 15% difference over salinity range) impact the effectiveness of dispersant A for the fresh or weathered PBC at any of the temperatures tested.
Presence of Ice: Not studied.
Energy Level: EPA Baffled Flask operated at 150, 200 and 250 rpm. Higher energy resulted in higher dispersion (all other factors constant)

Cox, J., L. Shultz 1981. Dispersant Effectiveness Under Arctic Conditions, Including Ice
Oil Type: Sadlerochit crude fresh, 10 and 30% weathered, 10% weathered Arctic diesel, 10% weathered Kuparuk crude
Dispersant Type: Identified as X,Y and Z only
Water Temperature: -0.6 °C
Water Salinity: 10, 20 and 32 ppt. results showed no difference in dispersant effectiveness over the range of salinities tested
Presence of Ice: 20 and 50% coverage of 1.5 cm thick and 5.7 cm diameter ice
Energy Level: MNS apparatus with ice present. Slight increase in natural dispersion with ice present versus open water. When dispersant was added dispersion rose substantially. No difference in results between 20% and 50% ice coverage

Fingas, M.F., I. Bier, M. Bobra and S. Callaghan. 1991. Studies on the Physical and Chemical Behaviour of Oil and Dispersant Mixtures
Oil Type: Alberta Sweet Mixed Blend, Norman Wells, Adgo
Dispersant Type: Corexit 9527, Enersperse 700 and Citrikleen

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Water Temperature: 0 to 50 °C on a subset of tests with Corexit 9527 and ASMB oil only. Dispersant effectiveness reduced with decrease in temperature.
Water Salinity: Maximum effectiveness was achieved at 40 to 45 ppt and fell sharply with either a decrease or increase in salinity for all dispersant and oil combinations tested.
Presence of Ice: Not studied
Energy Level: SF test with no variation in energy level

Fingas, M., B.Fieldhouse, Z.Wang. 2005b. The Effectiveness of Dispersants under Various Temperature and Salinity Regimesingas
Oil Type: Alberta Sweet Mixed Blend (ASMB)
Dispersant Type: Corexit 9500
Water Temperature: 0 to 25 °C on ASMB oil only. Dispersant effectiveness reduced with temperature increase above 20 °C and was similar over 5 to 20 °C contrary to most other research.
Water Salinity: Maximum effectiveness was achieved at 25 ppt and fell sharply with a decrease below 20 °C.
Presence of Ice: Not studied
Energy Level: SF test with no variation in energy level

Fingas, M., B. Fieldhouse, Z. Wang. 2006. The Effectiveness of Dispersants on Alaska North Slope Crude Oil under Various Temperature and Salinity Regimes
Oil Type: Alaska North Slope Crude (ANS)
Dispersant Type: Corexit 9500
Water Temperature: 5 to 25 °C Dispersant effectiveness reduced with temperature increase above 10 °C and was similar over 5 to 10 °C contrary to most other research where higher temperatures usually result in higher dispersant effectiveness.
Water Salinity: Maximum effectiveness was achieved at 25 ppt at all temperatures and fell sharply with water salinity below 20 ppt.
Presence of Ice: Not studied
Energy Level: SF test with no variation in energy level

Fiocco, R.J., P.S. Daling, G. DeMarco, R.R. Lessard, 1999. Advancing laboratory/field dispersant effectiveness testing
Oil Type: Alaska North Slope weathered oil and emulsions
Dispersant Type: Corexit 9500
Water Temperature: 15 °C
Water Salinity: 32 ppt assumed
Presence of Ice: Not studied
Energy Level: MNS test was run for longer duration (60 minutes from 5) to test Corexit 9500's ability to break emulsions. Successfully dispersion of emulsions measured with viscosities up to 15,000 cP and 65% water content. These data were compared to the 1997 North Sea field trial data where similar results were measured in the field for dispersion of emulsions by Corexit 9500.

George-Ares, A., R.R. Lessard, K.W. Becker, G.P. Canevari and R.J. Fiocco. 2001. Modification of the Dispersant Corexit 9500 for Use in Freshwater

Oil Type: Alaska North Slope Crude (ANS) plus 3 other South American crudes
Dispersant Type: Corexit 9500, calcium chloride modified 9500, Dasic freshwater, Enersperse 1037, Inipol IPF
Water Temperature: not reported, assumed room temperature and not varied
Water Salinity: All tests conducted using river (0 ppt) or deionized water. Corexit 9500 was modified by blending in calcium chloride solution at various concentrations (concentrations not reported) and tested with ANS crude oil. Conventional Corexit 9500 had an efficiency of 22% in fresh water. The modified Corexit 9500 had measured efficiencies of 29 to 63% depending on the quantity of calcium chloride added. Dasic fresh water was the most effective dispersant on all of the oils tested in the fresh water
Presence of Ice: Not studied
Energy Level: EXDET test with no variation in energy level

Lewis, A., A. Crosbie, L. Davies, T. Lunel. 1998. Large scale field experiments into oil weathering at sea and aerial application of dispersants.
Oil Type: Forties Blend, Alaskan North Slope crude, and IFO-180 fuel oil. ANS was emulsified to 35% water content prior to spraying
Dispersant Type: Corexit 9500 and Dasic Slickgone NS
Water Temperature: 18 °C
Water Salinity: full ocean salinity North Sea
Presence of Ice: Not studied
Energy Level: offshore conditions in 3 to 5 m/s winds with gusts 7 to 8 m/s. 30 m^3 of ANS crude, weathered for 55 h, was completely dispersed with Corexit 9500 applied from the air in two stages with a total DOR of approximately 1:12.

Li, Z., K. Lee, T. King, M. Boufadel, A. Venosa. 2009. Evaluating Crude Oil Chemical Dispersion Efficacy in a Flow-Through Wave Tank Under Regular Non-Breaking Wave and Breaking Wave Conditions
Oil Type: fresh ANS and weathered (14%) Mesa crude oil
Dispersant Type: Corexit 9500 & Dispersit SPC 1000
Water Temperature: not reported
Water Salinity: not reported
Presence of Ice: Not studied.
Energy Level: EPA /DFO wave tank operated with regular non-breaking waves, and plunging breakers. 21 to 36% of oil was dispersed and diluted with dispersants and non-breaking waves. 42 to 62% of the oil was dispersed and diluted with dispersants and plunging breakers. With no dispersants and both wave conditions only 8 to 19% of the oil was dispersed and diluted in the flow through wave tank. Drop sizes were large with regular waves and no dispersant (VMD > 300 um) and small with dispersants and breaking waves (VMD < 50 um).

Mackay, D. , R. Mascarenhas, K. Hossain, T. McGee. 1979. The Effectiveness of Chemical Dispersants at Low Temperatures and in the Presence of Ice.
Oil Type: Alberta Sour Mixed Blend and Lago Medio crude
Dispersant Type: Corexit 9527

Water Temperature: 0 to 15°C. It was concluded that the primary effect of water temperature was to lower the oil temperature and thus increase the oil viscosity. The increased oil viscosity reduced the dispersant effectiveness.
Water Salinity: 35 ppt
Presence of Ice: Ice was introduced into the hoop tank test apparatus. The effect of the ice was to dampen the waves and generally reduce effectiveness but no other significant conclusions could be drawn about the effects of the ice.
Energy Level: MNS, Hoop tank , and Calm Sea Simulation Apparatus: Hoop tank used in ice studies.

Mackay, D., Chau, Y. Poon. 1986. MNS, Rotating Flask and Hoop Tank Test Results
Oil Type: The effectiveness of was tested on Prudhoe Bay crude oil along with 11 other oils using both the MNS and a rotating flask (RF) test. The Prudhoe Bay crude dispersibility was generally higher than the average of the 12 oils tested indicating that this Alaskan oil was amenable to chemical dispersant use.
Dispersant Type: Corexit 9527, Corexit 9550 and BP MA700
MNS test results of the three dispersants tested on the Prudhoe Bay crude oil Corexit 9550 had the best performance at 71% followed by Corexit 9527 at 45.9% and BP MA 700 at 43.1%.
Water Temperature: 5 to 25° C
Study conclusions: 'There is no inherent reason to suggest that cold climate dispersion is significantly less feasible than temperate dispersion'.
'dispersion is likely to require more dispersant under these cold conditions but the extra amount is unlikely to be large except when the oils are unusually viscous, close to their pour point or waxy'.
Water Salinity: Study conclusions: 'when assessing the suitability of dispersants for use in variable salinity waters there is presently no alternative but to measure the magnitude of the salinity dependence of dispersion on a case by case basis'. The effect of salinity was most notable for Corexit 9527 in this work when compared to Corset 9550 and BP MA700. Since Corexit 9527 (and its more modern sister Corexit 9500) are the primary dispersants in use in Alaska this would suggest that water salinity may be a concern with this particular dispersant formulation.
Presence of Ice: Not investigated
Energy Level: Acknowledged the need to measure both mixing level that generates oil drops as well as the water column suspension energy. Ranked the mixing energies of the various test methods used but only speculated how these would compare to oceanic mixing levels

Mackay, D. 1995. Effectiveness of chemical dispersants under breaking wave conditions
Oil Type: Alaska North Slope weathered 5 to 20%
Dispersant Type: Corexit 9527
Water Temperature: 4.4 to 15.5 °C Increasing temperature resulted in a slight loss of effectiveness
Water Salinity: 0 to 32 ppt. The water salinity did not affect the dispersibility of the weathered ANS in the 5 to 32 ppt range in the EXDET test (this is contrary to other test results). 30 ppt in Esso wave basin.
Presence of Ice: Not studied

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Energy Level: MNS, WSL, EXDET and ESSO wave basin. EXDET was small scale test chosen as being representative, quick, more reproducible and with less waste water. EXDET energy level between 10 to 16 mm amplitude did not affect results. In the turbulent wave conditions of the wave tank (15 cm amplitude 2.5 s period) effectiveness was 90 to 100% at DORs of 1:100 with significant dispersion at DORs of 1:200 and 1:300
Other Results: The author calculated how much of the Exxon Valdez oil spill might have been dispersed if the dispersant available at the time of the spill had been applied. Determined that 38% of the oil could have been dispersed.

McAuliffe, C., B. Steelman, W. Leek, D. Fitzgerald, J. Ray, C. Barker. 1981. 1979 Southern California dispersant treated research oil spills.
Oil Type: Alaska Prudhoe Bay crude
Dispersant Type: Dispersant products identified as H & J (no brand names provided)
Water Temperature: not reported. Offshore Long Beach California in September (warm water)
Water Salinity: full ocean salinity (32 ppt)
Presence of Ice: Not studied
Energy Level: Wind speed or wave heights not reported. Extensive water sampling and analysis was undertaken and significant oil was identified in the water column up to 9 m depth. Dispersant was visually very effective as well.
Results Summary: ANS Oil was dispersible by both products but dispersant H was more effective, as measured by chemical analysis of water samples under the slick. Between 5 to 78% dispersion was measured. When dispersant was applied to the thick oil rather than entire slick dispersant effectiveness values of 60 to 78% were measured. Two hour weathered crude was less dispersible than freshly treated oil.

Moles, A.L. Holland, J. Short, 2001. Effectiveness of Corexit 9527 and 9500 in Dispersing Fresh, Weathered and Emulsion of Alaska North Slope Crude Oil Under Subarctic Conditions
Oil Type: Studied Alaska North Slope Crude (ANS) fresh, weathered and emulsified. Neither dispersant was effective on the weathered oil under any conditions tested.
Dispersant Type: Corexit 9527 and 9500. Comparable results were achieved with the two dispersants. Dispersant was pre-mixed with the oil and emulsions. This may have been one of the reasons for the high effectiveness values recorded for the emulsions.
Water Temperature & Water Salinity: 3, 10 and 22°C and 22 and 32 ppt
In tests using pre-mixed Corexit 9500 and 9527 dispersants and fresh ANS crude oil in the swirling flask test dispersion was not affected by salinity (22 ppt versus 32 ppt) at high temperatures (22°C) but was at low temperatures (10°C). Dispersion levels for fresh ANS were below the detectable limits of the SF test at 3°C and both salinities for both dispersants. Authors concluded that temperature, salinity and weathering are important factors to consider when evaluating the effectiveness of dispersants with weathering having the most profound effect. The effectiveness of 9500 in 32 ppt salinity water was similar at 10 °C and 22 °C. The colder water tests with 9527 and 32 ppt salinity had lower effectiveness.
Presence of Ice: Not studied
Energy Level: Author states that the swirling flask test is a conservative test that applies relatively low mixing energy.

Moles, A., L. Holland, J. Short. 2002. Swirling Flask Test Results
Oil Type: Alaska North Slope Crude (ANS) fresh, weathered and emulsified.
Dispersant Type: Corexit 9527 and 9500. Similar results were achieve with the two dispersants. Dispersant was pre-mixed with the oil and emulsions. This may have been one of the reasons for the high effectiveness values recorded for the emulsions.
Water Temperature & Water Salinity:
In tests using pre-mixed Corexit 9500 and 9527 dispersants and ANS crude oil in the swirling flask test dispersion was not affected by salinity (22 ppt versus 32 ppt) at high temperatures (22°C) but was at low temperatures (10°C). He concluded that temperature, salinity and weathering are important factors to consider when evaluating the effectiveness of dispersants with weathering having the most profound effect. The effectiveness of 9500 in 32 ppt salinity water was similar at 10 °C and 22 °C. The colder water tests with 9527 and 32 ppt salinity had lower effectiveness.
Presence of Ice: Not studied
Energy Level: Author acknowledges that the low energy level in the swirling flask test may not be a good representation of environmental conditions

Nagarajan, K., N. Deshpande, G. Sorial, J. Weaver. 2008. Dispersant Effectiveness on Oil Spills- Empirical Correlations.
Oil Type: Alaskan Prudhoe Bay (PBC) fresh, 10% and 20% evaporated, South Louisiana crude oil (SLC) fresh, 10% and 20% evaporated, No. 2 Fuel Oil (2FO) fresh, 3.8% and 7.6% evaporated. A linear, empirical correlation between effectiveness in BF test and all parameters tested (salinity, viscosity (as a combined measure of weathering and temperature effect) and rotational speed). Final correlation parameters not reported in paper.
Dispersant Type: Dispersants identified as A (Corexit 9500) & B (Dispersit SPC 1000)
Water Temperature: 5, 10, 16, 22, 27 and 35 °C. Highest effectiveness at 250 rpm for the most weathered PBC was achieved at 22 °C.
Water Salinity: 10, 20, 34 ppt. Salinity did not significantly (less than 15% difference over salinity range) impact the effectiveness of dispersant A for the fresh or weathered PBC at any of the temperatures tested.
Presence of Ice: Not studied.
Energy Level: EPA Baffled Flask operated at 150, 200 and 250 rpm. Higher energy resulted in higher dispersion (all other factors constant), 10% evaporated PBC was shown to be effectively 80+%) dispersed at the medium and high energy levels.

Nedwed, T. , R. Belore, W. Spring, D. Blanchet. 2007. Basin scale testing of ASD icebreaker enhanced chemical dispersion of oil spills
Oil Type:. Chayvo Z6, 3 to 6% weathered by weight
Dispersant Type: Corexit 9527. Dispersant applied to oil either prior to energy addition in broken ice or oil on ice tests or after ice breaker had broken ice and exposed the oil for treatment.
Water Temperature: Air temp 0 to -10 °C
Water Salinity: 32 ppt
Presence of Ice: Ice present in 25% to 100% ice sheet. Oil spilled in broken ice, on top of a full ice sheet and under a full ice sheet.
Energy Level: SL Ross wave tank with trolling motor prop wash. Greater than 90% effectiveness in ice cover ranging from 25% to 90%. Low dose (1:110 also effective. Prop wash

was effective on oil weathered for 98 hours. In AKER ice basin tests all energy was provided by the prop wash of a scale model azimuthal stern drive icebreaker. Dispersant effectiveness values of between 70% and 97% were measured in the tests. Oil drop VMD (d50) of 10 to 75 μm were measured in the tests indicating effective long term dispersion. Oil did not clear the tank after many weeks of sitting with no energy addition indicating long term dispersion even under quiescent conditions.

Owens, C.K.R. Belore, 2004. Dispersant effectiveness testing in cold water and brash ice.
Oil Type: Alaska North Slope, Hibernia, Chayvo crudes fresh and evaporated
Dispersant Type: Corexit 9527
Water Temperature: -0.6 to 0.9 °C
Water Salinity: 32 ppt
Presence of Ice: Yes, brash ice in 4/10 and 8/10 coverage. Higher dispersion was evident in the tests with ice cover when compared to open water at the non-breaking wave, low energy conditions tested for both fresh and weathered ANS and Hibernia crude.
Energy Level: Two wave settings used. Low: 17 cm average wave height with a 5.5 second period. High: 33 cm average wave height with a 4 second period. In low ice concentrations the higher mixing energy was needed to achieve the same dispersion as in the high ice cover, low energy tests.

Payne, J.R. et al. 1985. Estimating dispersant effectiveness under low temperature-low salinity conditions
Oil Type: Alaskan Prudhoe Bay crude oil
Dispersant Type: Corexit 9550, Finasol OSR-7, EC. O ATLANT'TOL AT-7, and OFC D-609 (AT-7 and OSR-7 were significantly less effective than others under all test conditions)
Water Temperature: 1 and 10 °C
Water Salinity: 0, 18 and 33 ppt. Corexit 9550 had best performance (>50% at 1°C, 42 % at 10 °C) at 0 ppt. D-609 outperformed Corexit 9550 at 18 ppt. Corexit 9550 and D-609 were equally effective at 33 ppt.
Presence of Ice: Not studied.
Energy Level: Used an old EPA protocol test (pre- Swirling Flask)

SL Ross. 2002. Dispersant Effectiveness Testing in Cold Water and Broken Ice
Oil Type: fresh and air sparged (evaporated) Alaska North Slope and Hibernia crude oil
Dispersant Type: Corexit 9500 & 9527.
Water Temperature: -0.5 to 2.4°C in open water -0.6 to 0.9°C in ice tests.
Water Salinity: 30 to 32 ppt
Presence of Ice: Broken ice with 50 % and 80% coverage. In open water tests DE of ANS fresh and weathered to 20% loss ranged from 96 to 99%. In ice cover tests DE of fresh and 10% weathered ANS in 8/10th ice >95%, for 20% weathered ANS DE was 22% with no ice, 30% with 4/10ths ice and 54% with 8.10ths ice. Presence of larger amounts of ice increased dispersion. DOR's ranged from 1:81 to 1:31.
Energy Level: Low energy swells (7.5 inch stroke and 10, 12 and 16 cycles /min) in ice tests, standard Ohmsett breaking waves (3.0 inch wave paddle stroke and 35 cycles per minute) in open water tests. DE in open water tests on fresh, 10% and 20% weathered ANS was >96% in all cases.

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SL Ross, MAR Inc. 2003. Dispersant Effectiveness Testing on Alaskan Crude Oils in Cold Water

Oil Type: fresh and air sparged ANS, Endicott, Northstar, Cook Inlet Middle Ground Shoals and Pt. McIntyre crude oils
Dispersant Type: Corexit 9500 & 9527. Ohmsett tests used only Corexit 9527.
Water Temperature: -1.1 to -0.4 °C. In Ohmsett tests Corexit 9527 was effective on all but two fresh and weathered oils at the low temperatures (74 to 86% DE). The 29% weathered Northstar and 11% weathered Endicott had DE of only 8% and 3%, respectively.
Water Salinity: 30 ppt
Presence of Ice: Not studied.
Energy Level: SL Ross wave tank tests and Ohmsett standard dispersant effectiveness test energy level with 3.5 inch paddle stroke and 34 cycles per minute. The SL Ross wave tank tests resulted in lower DE measurements for the fresh Endicott crude oil than the Ohmsett tests (8 to 33% versus 74% at Ohmsett) likely due to energy level differences.

SL Ross. 2006. Dispersant Effectiveness Testing On Water-In-Oil Emulsions At Ohmsett.

Oil Type: fresh, air sparged and emulsions of Endicott, IFO 30, IFO 120 and Sockeye crude
Dispersant Type: Corexit 9527 and 9500.
Water Temperature: 0.6 to 3.3°C at Ohmsett, 9°C in SLR tank. Fresh Endicott dispersed 66% in SLR tank: 6% weathered and emulsion 3 and 3.3% DE. On-tank formed Endicott emulsion (~4000 cP) dispersed 10 to 35%. Mechanically formed emulsion (~6000cP) 0 to 20% DE.
Water Salinity: 30 to 32 ppt
Presence of Ice: Not studied.
Energy Level: Ohmsett standard dispersant effectiveness test energy level with 3.5 inch paddle stroke and 34 cycles per minute. SL Ross wave tank standard dispersant effectiveness test wave energy.

SL Ross & MAR Inc. 2006b. Dispersant Effectiveness Testing in Cold Water on Four Alaskan Crude Oils

Oil Type: fresh, air sparged and on tank weathered ANS, Endicott, Northstar and Pt. McIntyre crude oils
Dispersant Type: Corexit 9527.
Water Temperature: 2.8 to -2.8 °C. Dispersant was effective on all fresh and weathered oils at the low temperatures (85 to 99% DE). Weathered oil effectiveness was much higher in the 2006 vs 2003 test series possibly due to oil property differences (pour point issue?)
Water Salinity: 30 ppt
Presence of Ice: Not studied.
Energy Level: Ohmsett standard dispersant effectiveness test energy level with 3.5 inch paddle stroke and 34 cycles per minute

SL Ross, MAR Inc. 2009. Low-Dose Repeat-Application Dispersant Testing

Oil Type: ANS, Endicott, Oseberg, Rock, Ewing Bank crude oils and IFO 30 fuel oil
Dispersant Type: Corexit 9500 applied in repeat (up to 5 passes) applications of small doses (aircraft application rate) similar cumulative dispersion with multiple small doses compared to one single high dose. DE for the two Alaskan oils ranged from 88 to 95%.

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Water Temperature: 16 to 18°C.
Water Salinity: 30 ppt
Presence of Ice: Not studied.
Energy Level: SL Ross Wave tank and Ohmsett standard effectiveness tests, 3.5 inch stroke, 34 cycles/minute.

SL Ross. 2010. Literature Review of Chemical Oil Spill Dispersants and Herders in Fresh and Brackish Waters
Oil Type: various including Alaska North Slope crude
Dispersant Type : various
Water Temperature: various
Water Salinity: 0 to 40 ppt. Review concluded that dispersants designed for use in marine waters are less effective when salinity falls below 20 ppt or rises above 40 ppt. Fresh water formulations work better in fresh water conditions but provide best results in water with salinities between 10 and 20 ppt
Presence of Ice: Not studied
Energy Level: Not studied

SL Ross, MAR Inc. 2011. Comparison of Large-Scale (Ohmsett) and Small-Scale Dispersant Effectiveness Test Results
Oil Type: Endicott, ANS plus 12 other crude oils
Dispersant Type: Corexit 9500
Water Temperature: 14 to 16°C. Endicott was 95% dispersed with 1:22 DOR at Ohmsett
Water Salinity: 30 to 32 ppt
Presence of Ice: Not studied.
Energy Level: Ohmsett standard dispersant effectiveness test energy level with 3.5 inch paddle stroke and 34 cycles per minute. WSL, Exdet, SF and BF
Fresh Endicott: Ohmsett DE 95%,WSL 27%, BF 80%, SF 62%, Exdet 86%
Endicott 19% evap. : Ohmsett DE 94%,WSL 18%, BF 72%, SF 42%, Exdet 90%
ANS fresh: Ohmsett DE 98%,WSL 28%, BF 76%, SF 67%, Exdet 92%
ANS 0% evap.: Ohmsett DE 97%,WSL 27%, BF 82%, SF 49%, Exdet 88%

Smith, D., G. Holliday. 1979. API/SC-PCO Southern Californian1978 Oil Spill Test Program
Oil Type: Alaska North Slope Crude
Dispersant Type: code named H & J
Water Temperature: warm water
Water Salinity: full ocean salinity
Presence of Ice: Not studied
Energy Level: natural offshore conditions in 4 to 18 knots
Results Summary: ANS Oil was dispersible by both products.

Sorial, G.A.K.M. Karen, H. Edith, A.D. Venosa, D.W. King. 2001. Development of a rational oil spill dispersant effectiveness protocol
Oil Type: Alaskan Prudhoe Bay and South Louisiana crude oil
Dispersant Type: 18 dispersants tested, results not tied to specific dispersant

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Water Temperature: assumed to be EPA standard temp of 23 ± 3 °C
Water Salinity: synthetic sea water (salinity not reported but assumed to be BF standard of 34 ppt)
Presence of Ice: Not studied.
Energy Level: Swirling Flask and EPA Baffled Flask. Baffled Flask results were more reproducible than SFT and resulted in a significantly higher estimate of dispersant effectiveness for a given oil and dispersant combination. Higher effectiveness is attributed to a higher mixing energy in the BF test. The fresh Prudhoe Bay crude oil tested was highly dispersible in the BF tests (>80%) by 10 of the 18 dispersants tested

Sørstrøm, S.E., Per Johan Brandvik, I. Buist, P. Daling, D. Dickins, L. Faksness, S.Potter, J. Rasmussen and I. Singsaas.2010. Joint industry program on oil spill contingency for Arctic and ice covered waters: Summary Report
Oil Type: Troll B, 30 min weathered on water prior to dispersant application, 6 hour weathered, 6 and 7 day weathered
Dispersant Type: Corexit 9500 , Dasic Slickgone NS
Water Temperature: Not reported but in the presence of an ice field: ~ -1°C.
Water Salinity: not reported
Presence of Ice: Yes. Field ice coverage of 70-80%, 80-90%.
Energy Level: Low natural energy situation at pack ice edge. Energy applied by boat thrusters and high pressure water jets after dispersant application. Dispersant efficiency was estimated to be > 90% in all three tests. Oil drop sixes measured were in the 5 to 30 um range.

Strom-Kristiansen, T., P.S. Daling, A. Lewis, A.B. Nordvik. 1994. *IFP, WSL and MNS Testing*
Oil Type: Alaska North Slope, Brent Blend, Murban, Bonny Light
Dispersant Type: Corexit 9527 and 9554 and Enersperse 700 on a full range of oil properties and emulsions. Other dispersants were screened using IFP test on 200°C weathered oil
Water Temperature: All tests conducted on ANS at 13 °C
Water Salinity: All tests on ANS at 35 ppt
Presence of Ice: Not studied
Energy Level: Both IFP and MNS tests used on a range of weathered ANS oils. WSL was used on oil residues collected from meso-scale weathering tank. The ANS crude was dispersible until weathered to a viscosity of about 2 to 3000 cP. The MNS test resulted in higher DE estimates than the IFP test. Fifty percent water content emulsions of weathered ANS were dispersed with similar DE as the weathered ANS. Meso-scale (recirculating flume) weathering and dispersant effectiveness tests (using WSL and IFP tests on oil collected from the flume) were also conducted on ANS. After 4 hours of weathering the IFP test estimated 63% effectiveness after 48 hours the WSL test estimated 24% DE on oil that had lost 42% by weight and was a 69% water content emulsion.

Spring, W, T. Nedwed, R. Belore.2006. Icebreaker Enhanced Chemical Dispersion of Oil Spills.
Oil Type: Chayvo Z6, 3 to 12% weathered by weight
Dispersant Type: Corexit 9527. Dispersant applied to oil either prior to energy addition in broken ice or oil on ice tests or after ice breaker had broken ice and exposed the oil for treatment.

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Water Temperature: Air temp 0 to -10 °C
Water Salinity: 32 ppt
Presence of Ice: Ice present in 0% to 100% ice sheet. Oil spilled in broken ice, on top of a full ice sheet and under a full ice sheet.
Energy Level: SL Ross wave tank with trolling motor prop wash tests resulted in greater than 90% effectiveness in ice cover ranging from 25% to 90%. With prop wash. Waves only tests with dispersant generated 40 to 56% effectiveness. Low dose (1:110 also effective. Prop wash was effective on oil weathered for 98 hours. In AKER ice basin tests all energy was provided by the prop wash of a scale model azimuthal stern drive icebreaker. Dispersant effectiveness values of between 94% and 97% were measured in the tests. A control test with no dispersant applied resulted in DE of <20 %.Oil drop VMD (d50) of 17 to 45 µm were measured in the tests indicating effective long term dispersion. Oil did not clear the tank after many weeks of sitting with no energy addition indicating long term dispersion even under quiescent conditions.

Venosa, A.D.G.A. Sorial, D.W. King. 2001. Round-robin testing of a new EPA dispersant effectiveness protocol.
Oil Type: Alaskan Prudhoe Bay and South Louisiana crude oil
Dispersant Type: Six dispersants tested, results not tied to specific dispersant
Water Temperature: assumed to be EPA standard temp of 23 ± 3 °C
Water Salinity: synthetic sea water (salinity not reported but assumed to be BF standard of 34 ppt)
Presence of Ice: Not studied.
Energy Level: EPA Baffled Flask. Eight different labs used the Baffled Flask test to determine inter-laboratory variability in testing with this method. It was found that the BF test was much more reproducible and repeatable than the SF test. The effectiveness of the 6 dispersants on fresh Prudhoe Bay crude varied widely from a low of 10% to a high of 89%

Venosa, A., K. Lee, M. Boufadel, Z. Li, E. Wickley-Olsen, T. King, 2008. Dispersant Effectiveness as a Function of Energy Dissipation Rate in an Experimental Wave Tank.
Oil Type: fresh ANS and weathered Mesa
Dispersant Type: Corexit 9500 & Dispersit SPC 1000
Water Temperature: not reported
Water Salinity: not reported
Presence of Ice: Not studied.
Energy Level: EPA /DFO wave tank operated with regular waves, spilling and plunging breakers. Measured energy dissipation rate was similar to field measurements. Both dispersants were effective on the ANS but the Dispersit product required higher energy to achieve same dispersion as Corexit 9500.

White, D.M.; Ask, I.; Behr-Andres, C. 1999. Final Report: Effectiveness Testing for Corexit 9500 on Alaska North Slope Crude Oil in Prince William Sound Seawater at 8°C.
Oil Type: Alaska North Slope crude
Dispersant Type: Corexit 9500. Higher dose rate higher dispersant effectiveness.
Water Temperature: 8 °C.
Water Salinity: PWS sea water (31 to 32 ppt).
Presence of Ice: Not studied.

Energy Level: modified SFT and modified EXDET (no sorbent and same extraction analysis as in SF test). Energy added 0, 12, 24, and 48 hrs after dispersant was applied. Oil was also allowed to 'weather' in the test flask between 0, 12, 24, 48, or 72 hours before dispersant application. Highest dispersion occurred with zero weathering and dispersant contact greater than 0. Lowest dispersion occurred with 0 contact time across all weathering. If oil weathers it is less dispersible. If dispersant does not have a chance to mix with oil before energy is applied, poor dispersion.

Wrenn, B., A. Virkus, B. Mukherjee, A. Venosa. 2009. Dispersibility of crude oil in fresh water. Environmental Pollution 157 (2009) 1807-1814.

Oil Type: weathered Mars crude
Dispersant Type: various experimental formulations
Water Temperature: not reported, assumed room temperature and not varied
Water Salinity: All tests conducted using fresh (0 ppt) water. Objective was to develop a dispersant formulation that would provide good effectiveness in fresh water. Objective was met for the single oil tested but authors indicate many other oils would need to be tested to ensure that the dispersant formulation worked over a range of oils
Presence of Ice: Not studied
Energy Level: EXDET test with no variation in energy level.

ED_001324_00000589-00103

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Campo-Moreno, Pablo (campomp)
Sent: Mon 1/26/2015 6:51:41 PM
Subject: Fwd: Current Status of biodegradation dispersed oil and dispersants
current status.docx

Hope this helps,
Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
PH:(513)-556-3637
Fax: (513)-556-4162
campomp@ucmail.uc.edu

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.
The adventures for Sherlock Holmes

Begin forwarded message:

From: "Zhuang, Mobing (zhuangmg)" <zhuangmg@mail.uc.edu>
To: "Campo-Moreno, Pablo (campomp)" <campomp@UCMAIL.UC.EDU>
Subject: Current Status of WA 33
Date: January 26, 2015 at 1:43:23 PM EST

Hi Pablo,

Please see the attachment. Let me know if there is any problem, thanks!

Regards,
Mobing Zhuang

PH.D Candidate

Department of Environmental Engineering
University of Cincinnati
Cin

cinnati, OH 45221

To: Conmy, Robyn[Conmy.Robyn@epa.gov]
Cc: Raghuraman Venkatapathy[raghuraman.venkatapathy@ptsied.com]; Holder, Edith[holder.edith@epa.gov]; BOL-Deshpande, Ruta (deshpars)[deshpars@mail.uc.edu]; BOL-Zhang, Yu (zhang4y5)[zhang4y5@mail.uc.edu]
From: Campo-Moreno, Pablo (campomp)
Sent: Thur 6/4/2015 12:11:34 PM
Subject: Re: Finasol and dilbit results

No problem. Let's meet on Monday at 10 am
Regards

Pablo

On Jun 4, 2015, at 07:50, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

> Yes, the building is shut down. Can we reschedule for Monday morning?
>
> Sent from my iPhone
>
> On Jun 4, 2015, at 6:21 AM, Raghuraman Venkatapathy <raghuraman.venkatapathy@ptsied.com> wrote:
>
>> Pablo,
>>
>> The meeting will likely be cancelled as the main building is still closed (no power since yesterday morning).
>>
>> Thanks,
>> raghu
>>
>> ---
>> Raghuraman Venkatapathy
>> On-Site Technical Manager
>> Pegasus Technical Services, Inc.
>> On-Site Contractor to U.S. EPA
>> NRMRL-STD, MS:443
>> 26 W. Martin Luther King Jr. Drive
>> Cincinnati, OH 45268.
>> Phone: (513) 569 7077(O)/(513) 549 7880(GV)
>> Fax: (513) 569 7677
>> e-mail: raghuraman.venkatapathy@ptsied.com
>> venkatapathy.raghuraman@epa.gov
>>
>> On 06/02/2015 10:35 AM, Campo-Moreno, Pablo (campomp) wrote:
>>
>>> Works for me. See you on Thursday at AWBERC
>>> Regards,

Pablo Campo-Moreno, Ph.D.

Research Assistant Professor
University of Cincinnati
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On Jun 2, 2015, at 10:33 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

OK. How about Thursday morning at 10?

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Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

513-431-1970 (EPA mobile)

727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Campo-Moreno, Pablo (campomp)
[mailto:campomp@UCMAIL.UC.EDU]
Sent: Tuesday, June 02, 2015 10:30 AM
To: Conmy, Robyn
Cc: Holder, Edith; BOL-Deshpande, Ruta (deshpars); BOL-Zhang, Yu (zhang4y5); Venkatapathy Raghuraman
Subject: Finasol and dilbit results

Dear Robyn,

Hope you're doing all right. We finished the biodegradation experiment with Finasol and completed the analysis of the ANS and dilbit samples Edie sent us. I'd like to meet with you at your earlier convenience to discuss our results. This week I'm available any time but Wed from 9 am to 2 pm.

Regards,

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To: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Campo-Moreno, Pablo (campomp)
Sent: Mon 5/11/2015 6:28:16 PM
Subject: Re: dilbit biodegradation

Sure!
Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
766 ERC
Cincinnati, OH 45221-0012
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campomp@ucmail.uc.edu

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On May 11, 2015, at 2:24 PM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

OK, great. Let's plan for a meeting at the end of the mnth to go over the results.

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Robyn N. Conmy, Ph.D.

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727-692-5333 (Personal mobile)

conmy.robyn@epa.gov

From: Campo-Moreno, Pablo (campomp) [mailto:campomp@UCMAIL.UC.EDU]
Sent: Monday, May 11, 2015 11:40 AM
To: Conmy, Robyn
Cc: Venkatapathy Raghuraman
Subject: Re: dilbit biodegradation

Robyn,

Last Friday we had the last sampling event for the Finasol experiment. We already finished the DOSS analysis and we're injecting the oil extracts. If all the QA/QC checks pass, we can analyzed Edie's samples by Memorial day week.

Regards,

Pablo Campo-Moreno, Ph.D.
Research Assistant Professor
University of Cincinnati
Department of Biomedical, Chemical and Environmental Engineering
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Cincinnati, OH 45221-0012
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On May 11, 2015, at 6:53 AM, Conmy, Robyn <Conmy.Robyn@epa.gov> wrote:

Hi Pablo,

Do you have a date on when there will be results from the ongoing dilbit biodegradation experiments?

Thanks,

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

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conmy.robyn@epa.gov

To: Holder, Edith[holder.edith@epa.gov]
Cc: Conmy, Robyn[Conmy.Robyn@epa.gov]
From: Bryan, Elisha
Sent: Mon 4/20/2015 12:48:44 PM
Subject: Fw: ZI-400 sample inquiry

Hello Edie & Robyn,

I am forwarding this message from ZI Chemicals. I could email him back and tell him that a different group covers those decisions and to send all questions to the contact listed in the link. I wanted to double check with both of you first.

I am not sure how you want to handle purchasing either.

Thanks,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

26 W. Martin Luther King Dr.

Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

From: Barnaby Zelman <zichemicals@mac.com>
Sent: Friday, April 17, 2015 8:29 PM
To: Bryan, Elisha
Cc: inquiry@ZIChemicals.com
Subject: Re: ZI-400 sample inquiry

Dear Elisha,

The cost, including UPS Ground service delivery of a 1 quart sample of our ZI-400 Oil Spill Dispersant made to order for the EPA would be $85. If this is acceptable please advise if you can issue payment via ACH, Wire transfer, or check (our last preference)?

May I ask one question...I could not find after cursory review of the link you provided where it mentions how long of a transition period would be allowed [after rule adoption] for manufacturers such as us to develop, test, submit, and list, the new products we will need to comply with the proposed revisions? For what it's worth, for us, we would like 2-3 years to be able to get any new products on the EPA listing before our existing product is removed. It's a matter of financial survival for small businesses such as ours and we do hope the EPA remains sensitive to this as well, given your own report indicated that 90% of current listed products are made by small businesses.

Thank you very much and awaiting your reply soonest.

Best regards,

Barnaby Zelman
Z.I. Chemicals
zichemicals@mac.com

On Apr 16, 2015, at 12:43 PM, "Bryan, Elisha" <Bryan.Elisha@epa.gov> wrote:

Good Afternoon,

The U.S. Environmental Protection Agency will be conducting a series of Dispersant Efficacy experiments using the newly proposed Baffled Flask Test for inclusion in the 40 CFR Appendix C to Part 300 Subpart J. I am a contractor with EPA's Office of Research and Development, National Risk Management Research Laboratory (NRMRL), Land Remediation and Pollution Control Division (LRPCD), working on this research.

As your product is listed on the U.S. EPA National Contingency Plan Product Schedule, we would like to include your product in our research and are interested in procuring a small quantity. I am contacting all manufacturers listed so that we can take into consideration the different characteristics of the dispersants.

This research will not change the current status of your product on the Product Schedule. More information on the proposed revisions and who to contact for comments can be found here: https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan#h-44.

Could you please send me a price quote for one liter / quart of *ZI-400*?

Thank you,

Elisha Bryan

Pegasus Technical Services, Inc.

On-Site Contractor to the U.S. EPA

ORD/NRMRL/LRPCD

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Cincinnati, OH 45268

Phone: 513-965-4805

Email: bryan.elisha@epa.gov

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Cc: Holder, Edith[holder.edith@epa.gov]; BOL-Deshpande, Ruta (deshpars)[deshpars@mail.uc.edu]; BOL-Zhang, Yu (zhang4y5)[zhang4y5@mail.uc.edu]
From: Raghuraman Venkatapathy
Sent: Thur 6/4/2015 10:21:27 AM
Subject: Re: Finasol and dilbit results

Pablo,

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Thanks,
raghu

Raghuraman Venkatapathy
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Regards,

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