**To:** Sayles, Gregory[Sayles.Gregory@epa.gov]
**Cc:** Lindquist, Alan[Lindquist.Alan@epa.gov]
**From:** Magnuson, Matthew
**Sent:** Sun 1/26/2014 6:02:43 PM
**Subject:** Re: Glycol ethers and the WV spill

Greg,

I have a Cluster proposal review meeting from 10-2 tomorrow. I'll show up late if you think the WV call is worth it.

In looking at the invite list, it's a collection of organizations, so people might not be free to talk. If the call is recorded, i'd be interested in listening later.

I would offer the following;
1) Missing from the invite list is anyone from ORSANCO. The detection limit of their on-line monitors (some sort of GC) appeared to be better by 100x than the method supplied by the manufacturer for the cyclohexyl compound (the first one). If the gycol ether is an item of commerce, ORSANCO may have a good method for it already.

2). About a year ago, in talking with Jody Shoemaker from NERL upstairs, she said she was working on a frac material method. I don't know if she included this ether, but I can ask. From the email train below, i'm assuming this has been used in fracking.

3). I would interested if there is any discussion of chlorination products, which seem quite possible on the phenyl ether.

Thanks.
Matthew

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From: Sayles, Gregory
Sent: Sunday, January 26, 2014 10:08:22 AM
To: Magnuson, Matthew
Cc: Lindquist, Alan
Subject: Fw: Glycol ethers and the WV spill

Hi Matthew - I just forwarded an invite to the large analytical interest group supporting the WV effort. Brian Schumacher of NERL has been in the loop on this. I was thinking it might be helpful to include you as well. Let me know if you can be on with me. Thanks.

Greg

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From: Sayles, Gregory
Sent: Sunday, January 26, 2014 10:04:41 AM
To: Schumacher, Brian
Cc: Orme-Zavaleta, Jennifer; Gentry, Randall
Subject: Re: Glycol ethers and the WV spill

Brian - the large analytical group will be having a conference call tomorrow at 10 am eastern. I know that is early for you but I would appreciate you joining. I will forward the invite next. Feel free to add others on your end as you see fit - let me know if you do.

Thanks
Greg

From: Schumacher, Brian
Sent: Saturday, January 25, 2014 1:05:18 PM
To: Sayles, Gregory
Cc: Orme-Zavaleta, Jennifer; Gentry, Randall; Koglin, Eric
Subject: Re: Glycol ethers and the WV spill

Greg,

I saw that too. As a logical first choice, based on similar or related compounds, there are GC methods listed. However, their efficiency in seeing the glycol ethers is questionable if you want real quantitation.

As a related type of tale, we are looking at ethylene glycol now. SW-846 listed Method 8315 (I think) as having the ability to do EG in one version and then in the update, it is gone. Even the best extraction cartridges that we could find only listed a 40% capability. We found less recovery.

Makes me wonder what their spike recoveries were (if done) and did they adjust the data based on it.

Brian

From: Sayles, Gregory
Sent: Saturday, January 25, 2014 7:52:31 AM
To: Schumacher, Brian
Cc: Orme-Zavaleta, Jennifer; Gentry, Randall; Koglin, Eric
Subject: Re: Glycol ethers and the WV spill

Thanks, Brian. Fortuitously, R3 is the lead Region for this spill and so they should have that info at their fingertips. From one of the emails I sent you, it seems WV is using a GC method at this point.

Greg

From: Schumacher, Brian
Sent: Saturday, January 25, 2014 10:44:15 AM
To: Sayles, Gregory
Cc: Orme-Zavaleta, Jennifer; Gentry, Randall; Koglin, Eric
Subject: Re: Glycol ethers and the WV spill

Greg,

Yes, we verified the glycol and glycol ether method developed by the Region 3 laboratory (Jennifer Gundersen) as part of our HF research. The method is a direct inject LC/MS/MS method for groundwater (or cleaner) matrices. **Ex. 5 - Deliberative** via SPE. We looked at 2-Butoxy and 2-Methoxyethanols by the method.

Brian

From: Sayles, Gregory
Sent: Saturday, January 25, 2014 7:07:31 AM
To: Schumacher, Brian
Cc: Orme-Zavaleta, Jennifer; Gentry, Randall; Koglin, Eric
Subject: Glycol ethers and the WV spill

Brian -

As you may know, the WV spill challenge has turned to worry about glycol ethers that were in the leaking tank with the crude MCHM but were not known to be there until early this week. State of WV, R3 and CDC are working on getting analytical results with sufficiently low reporting levels.

CDC via NIEHS reached out to OW and ORD yesterday asking us any consultation help possible. I deferred to OW to check in with R3 and see what help they needed. So far, ORD has not been asked for direct support on this subject. However, I think we should be prepared so I want to bring you up to speed. Jennifer informed me that you worked with R3 on glycol ethers for HF.

I will now send you some email strings that will hopefully make sense in the whole. Please read through them. ORD was asked earlier for toxicology insights and so NCEA prepared a quick summary (here, below - see the attachment too that include the MSDS), and I asked Matthew Magnuson of NHSRC for his thoughts on treatment and fate - coming next.

Let me know if you have questions.

Thanks much.

Greg

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From: Kavlock, Robert
Sent: Wednesday, January 22, 2014 4:11:03 PM
To: Clark, Becki; Sayles, Gregory
Cc: Kadeli, Lek; Vandenberg, John; Blackburn, Elizabeth
Subject: FW: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom

Becki/Greg

Please find ORD comments on the hazards of PPH as prepared by NCEA staff at your request.

Bob

-----Original Message-----
From: Vandenberg, John
Sent: Wednesday, January 22, 2014 12:58 PM
To: Kavlock, Robert
Cc: Cogliano, Vincent
Subject: FW: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom
Importance: High

Bob,

Per our discussion:

The two MSDS we received this morning indicate the material is propylene glycol phenyl ether (DOWANOLTM PPH Glycol Ether) and a mixture of dipropylene glycol phenyl ether (>=60%), propylene glycol phenyl ether (<=25%), and polypropylene glycol phenyl ether (<=15%) (DOWANOLTM DiPPH Glycol Ether). I can't tell what mixture was actually released though the Freedom Industries sheet indicates "5.6% in MCHM" (handwritten notation, no identification of author).

It appears the larger component of the DIPPH Glycol Ether (e.g., dipropylene glycol phenyl ether CAS#051730-94-0) is used in household cleaning agents, though the percentage composition wasn't

included: http://householdproducts.nlm.nih.gov/cgi-bin/household/brands?tbl=brands&id=18001634

The MSDS include the statement for PPH Glycol Ether "Has caused birth defects in laboratory animals only at doses toxic to the mother". For DiPPH Glycol Ether the statement is "Contains component(s) which caused birth defects in laboratory animals only at doses toxic to the mother." I'd note that EPA's guidelines for developmental toxicity do not discount findings of developmental toxicity in the presence of maternal toxicity.

I looked for information via a simple internet search. I have not done a thorough search for information but it appears there are several unpublished studies available for some of these materials.

Notably, the California Air Resources Board created a draft interim REL in 2010 for propylene glycol phenyl ether. This is clipped from that report (entire report attached).

"Reproductive and Developmental Toxicity BASF Corporation (2000, unpublished report cited in OECD 2004) conducted a two-generation toxicity test in which 0, 100, 1000, or 5000 ppm (0, 11.3, 113.9, 477.5 mg/kg bw/day) PPh were administered in the drinking water to two generations of Wistar rats (25/sex/group) over an average of 26 weeks in parental generations. First generation rats (F0) received PPh 77 days prior to mating while the second parental generation (F1) received PPh for their lifetimes until termination. F0 and F1 reproductive performance were not affected at any dose. Estrous cycle, mating behavior, conception, gestation, parturition, lactation and weaning, as well as sperm parameters and sexual organ weights, and gross and histopathological findings of these organs were similar between control and treated animals. Signs of general systemic toxicity, characterized by decreased water and food consumption and decreased body weight and body weight gain were noted in F0 and F1 animals receiving the highest dose although pathology and histopathology did not reveal substance-related adverse effects. Pups of F0 and F1 parents receiving 5000 ppm PPh exhibited signs of developmental toxicity in terms of reduced body weight and body weight gain and delayed sexual maturation. NOAELs established in this study are as follows: reproductive performance and fertility NOAEL = 5000 ppm for F0 and F1 parents; developmental toxicity NOAEL = 1000 ppm for F1 and F2 progeny; general systemic toxicity NOAEL = 1000 ppm for F0 and F1 parents.

The following study by Hellwig and Hildebrand (1995, cited in OECD 2004) is in agreement with the BASF study above in demonstrating that PPh confers developmental toxicity at high doses that also produce toxicity in the dam.
Route of Exposure
Species, Dose/Exposure Levels
Oral (gavage)
Himalayan rabbit
0, 60, 180, 540 mg/kg-d
Gestation days 7 through 19

Results: Maternal Tox.
(NOAEL, LOAEL)
No effects at 0, 60, or 180
Decreased weight gain,
apathy at 540 mg/kg-d
NOAEL = 180 mg/kg-d
LOAEL = 540 mg/kg-d

Results: Offspring
(NOAEL, LOAEL)
No effects at 0, 60, or 180
Increased skeletal variation
(13th rib) at 540 mg/kg-d
NOAEL = 180 mg/kg-d
LOAEL = 540 mg/kg-d

Table adapted from OECD 2004."

The NOAEL indicated from this CARB report for propylene glycol phenyl ether is 180 mg/kg/day whereas

Ex. 5 - Deliberative

The other health effects are eye irritation and skin irritation, and nausea if swallowed. I didn't find additional information about these effects in my limited search.

Please let me know if additional information is needed.

John Vandenberg

-----Original Message-----
From: Sayles, Gregory
Sent: Wednesday, January 22, 2014 9:17 AM
To: Vandenberg, John; Cogliano, Vincent
Cc: Kavlock, Robert; Trovato, Ramona; Kadeli, Lek; Clark, Becki; Magnuson, Matthew
Subject: FW: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom
Importance: High

John, Vince - I spoke with Becki this morning. She is asking us for any thoughts we have based on these on these attached documents (and see the email string) - please send your comments to Becki and cc Chris Weis ASAP. Becki may pull us together on a call later today to discuss. In the meantime, I will ask Matthew Magnuson in NHSRC to look into treatment.

Thanks

Greg

-----Original Message-----
From: Clark, Becki
Sent: Wednesday, January 22, 2014 8:14 AM
To: Sayles, Gregory
Subject: Fw: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom
Importance: High

Here it is with the attachments.

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From: Weis, Christopher (NIH/NIEHS) [E] <christopher.weis@nih.gov>
Sent: Tuesday, January 21, 2014 6:29:43 PM
To: Clark, Becki
Subject: FW: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom

Becki,

I thought you should see this emerging information from the Elk River Spill. If you could share it with the EPA review team, I would appreciate it.

Thanks,

Chris

Christopher P. Weis, Ph.D., DABT
Toxicology Liaison/Senior Advisor
Office of the Director
National Institutes of Health
National Institute for Environmental Health Science
31 Center Street, Room B1C02
Bethesda, MD 20892-2256

PH: 301.496.3511

From: "Kapil, Vikas (CDC/ONDIEH/NCEH)" <vck3@cdc.gov<mailto:vck3@cdc.gov>>
Date: Tue, 21 Jan 2014 15:21:08 -0500
To: Christopher Weis <Christopher.Weis@NIH.gov<mailto:Christopher.Weis@NIH.gov>>
Subject: FW: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom

MSDSs attached….as discussed Chris. Please give me a call if you have thoughts….note the LD50 and some comments on cancer info.

Thanks again,

Vik

From: Werner, Lora S. (CDC epa.gov)
Sent: Tuesday, January 21, 2014 11:10 AM
To: Helverson, Robert (CDC epa.gov); Markiewicz, Karl (EPA) (CDC epa.gov); Cseh, Larry (ATSDR/DTHHS/OD); Kapil, Vikas (CDC/ONDIEH/NCEH); Holler, James S. (Jim) (ATSDR/DTHHS/OD); Murray, Ed (ATSDR/DTHHS/OD); Wheeler, John (ATSDR/DTHHS/OD); Welsh, Clement (ATSDR/DTHHS/OD)
Subject: Fw: Additional chemical was in Tank 396 with the MCHM that was leaked (Freedom

Please see below from EPA R3.

Ed, can Larry and your group review the tox info on this additional chemical for our internal purposes as soon as possible?

We can discuss this at our 4 pm with Robin and determine how to discuss with the state. I am sure at least their environmental state folks are also aware of this now too, and we can expect the health folks to ask our opinion soon is my guess.

Lora

From: Linden, melissa
Sent: Tuesday, January 21, 2014 10:55:45 AM
To: Burns, Francis; Kelly, Jack (R3 Phila.); Werner, Lora
Subject: Additional chemical was in Tank 396 with the MCHM that was leaked

Good morning,

During the 10am meeting with Freedom Industries this morning we were told that there was a mixture in Tank 396, instead of just MCHM. The mixture was approximately 5.6% of the PPH which can be found in the attached MSDS sheet from published by Freedom Industries. The PPH is a combination of the two products from DOW which are also attached to this email. Approximately 300 gallons of the PPH with 6251 gallons of MCHM for the total release (including what is still in the soil and what made it to the river).

Thanks,

Melissa Linden

On-Scene Coordinator

Western Response Branch (3HS32)

Hazardous Site Cleanup Division

1060 Chapline St. Suite 401

Wheeling, WV 26003

Phone: 304-234-0251

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From: Ex. 6 - Personal Privacy @TechLawInc.com>>
Sent: Tuesday, January 21, 2014 10:40 AM
To: sharma, raj; Linden, melissa
Subject: MSDS for PPH

Hello,

Attached, please find the three MSDS for the PPH.

Thanks,

Ex. 6 - Personal Privacy

Techlaw, Inc
2208 Warwood Ave
Wheeling, WV 26003

Ex. 6 - Personal Privacy

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