Hide Details

Resource Extraction Discharge Permitting Discussion with CDPHE

Wed 02/08/2012 11:30 AM - 1:00 PM

Attendance is **required** for Gail Franklin

Chair: **Kristen Keteles/R8/USEPA/US**

Location: Dakota

This entry has an alarm. The alarm will go off 1 hour before the entry starts.

Required:	Elaine Lai/R8/USEPA/US@EPA, Gail Franklin/R8/USEPA/US@EPA, Jim Lazorchak/CI/USEPA/US@EPA, Sandra Spence/R8/USEPA/US@EPA, Tina Laidlaw/MO/R8/USEPA/US@EPA, Tonya Fish/R8/USEPA/US@EPA

Description

site criterion_IC25_kc_revised.xlsx Region 8 Mayfly Presentation v3.pptx AECOM packet_fl.pdf

Meeting with Rami Naddy and CDPHE to discuss WET and permitting

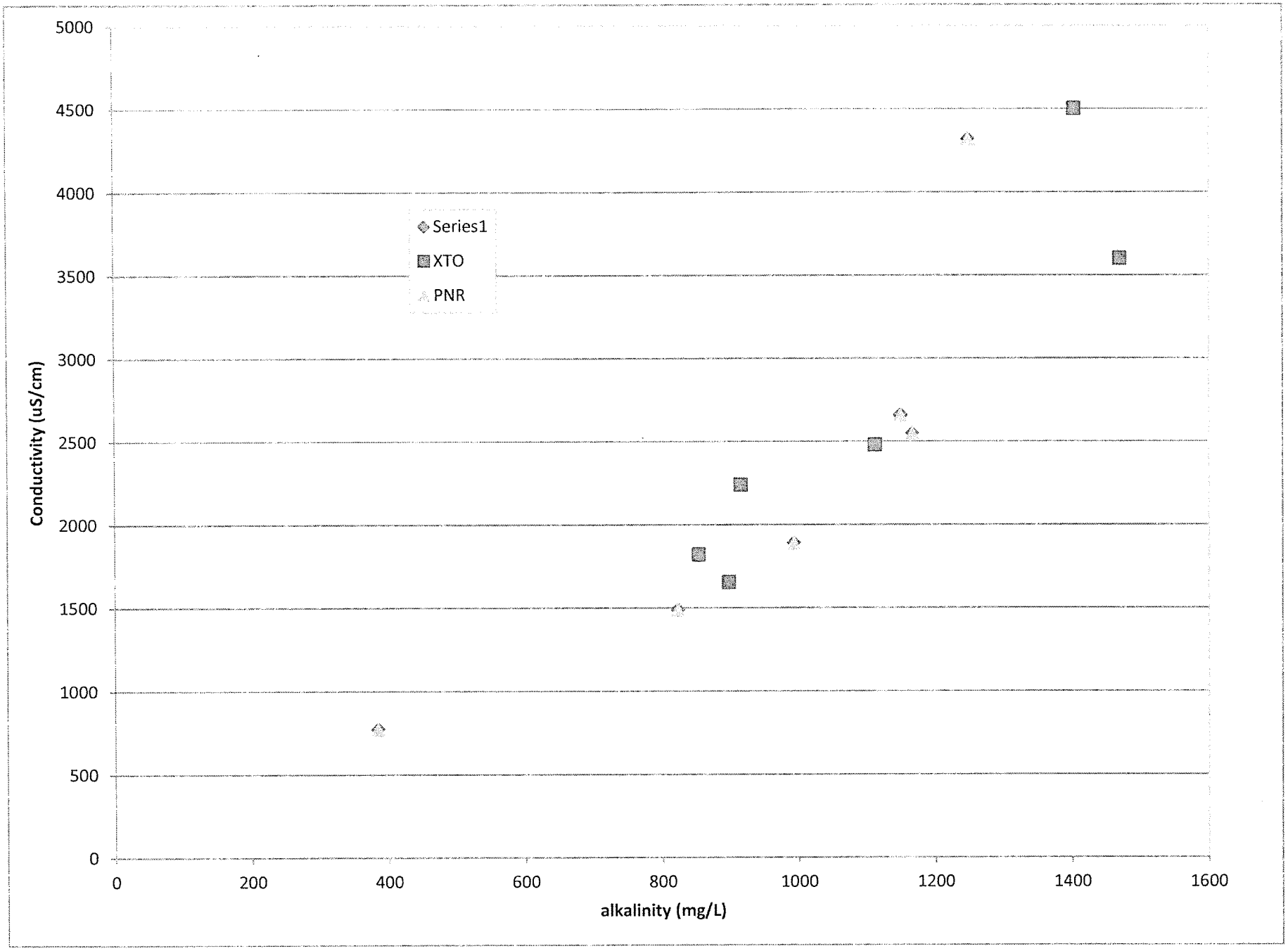
For those who can't be present: 866-299-9141 code 47498686 and slides are attached.

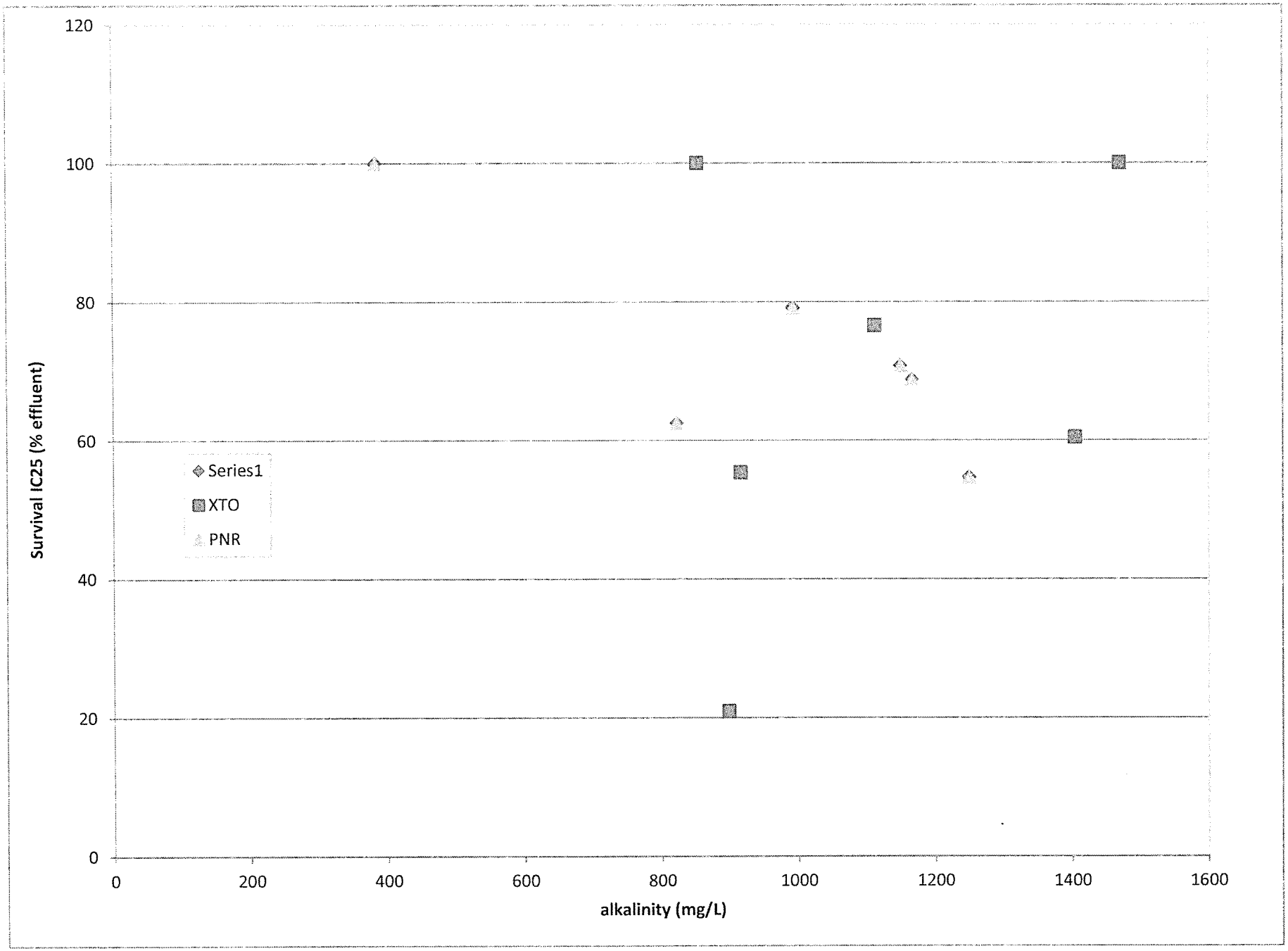
Personal Notes

Sites selected for further testing

	Facility/ Client	Location	Outfall	Date	Hardness (mg/L as CaCO3)	Alkalinity (mg/L as CaCO3)	Conductivity (umhos/cm)	TRC (mg/L)	Chloride (mg/L)	CC IC25 (Surv.)	Cd IC25 (Reprod)	Dm IC25 (Surv.)	Dm IC25 (Grwth)	Pp IC25 (Surv.)	Pp IC25 (Grwth)
	Sites toxic to *C. dubia*														
CO0048054	XTO Energy	Hill Ranch	036A	10/12/10	16	1404	4502 <	0.01	1290	60.42	9.3 >	100 >	100 >	100 >	100
CO0048054	XTO Energy	Hill Ranch	018A	3/22/11	20	916	2240 <	0.01	106	55.36	10.96 >	100 >	100 >	100 >	100
	XTO Energy	Hill Ranch	091A	9/9/10	48	1470	3602 <	0.01	254 >	100	5.61			67.86	67.33
	XTO Energy	Hill Ranch	025A	10/13/10	24	1112	2480 <	0.01	736	76.56	12.28	63.89	62.83 >	100 >	100
CO0048062	XTO Energy	COARLA05A	032A	6/29/11	12	898	1655		33.1	20.94	17.05 >	100 >	100 >	100 >	100
CO0048054	XTO Energy	Hill Ranch	082A	9/8/10	16	854	1820 <	0.01	55.5 >	100 >	100 >	100 >	100 >	100 >	100
	Pioneer	Kudzu	054	3/15/11	9.40	822.74	1490		54.55	62.50	38.35 >	100 >	100 >	100 >	100
	Pioneer	Milano	116	3/15/11	12.43	1149.12	2659		127.89	70.83	33.65 >	100 >	100 >	100 >	100
	Pioneer	Lorencito	022	4/5/11	36.64	1249.24	4321		496.46	54.69	37.3 >	100 >	100 >	100 >	100
	Pioneer	Lorencito	005	8/11/10	15.54	1166.11	2550		62.21	68.82	45.47			88.89	82.58
	Pioneer	Lorencito	059	4/12/11	8.98	992.94	1891		17.45	79.17	34.63	82.35	81.02 >	100 >	100
	Pioneer	Mitotes Lake	020	9/28/10	17.32	384.03	774		9.01 >	100 >	100	---	--- >	100 >	100
					Count	12									

Note: chemistry for PNR sites was taken from the maps provided by PNR / Aquat-tox (i.e., results of 5-yr avg).

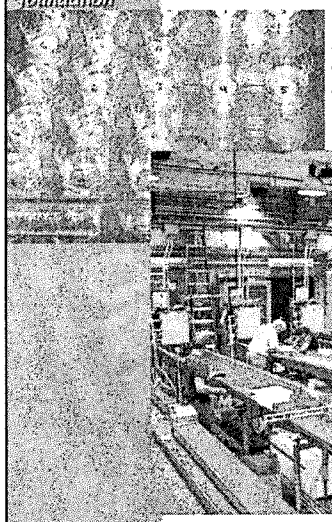

5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Conductivity (uS/cm)
0
200
400
600
800
1000
1200
1400
1600
alkalinity (mg/L)
Series1
XTO
PNR


120
100
80
60
40
20
0
Survival IC25 (% effluent)
0
200
400
600
800
1000
1200
1400
1600
alkalinity (mg/L)
Series1
XTO
PNR

RESEARCH & DEVELOPMENT

Building a scientific foundation

Methods - TDS MESOCOM Study



Beakers for exposure on the bench

Stream Mesocosms

1. Run single organism tests in WET framework
2. Simulate ecoStructure-Function to understand the role and response of small streams to changing nature of Point Sources.
3. Study abiotic/biotic interactions as determinants of the role of small stream ecosystems in sustainable water management

RESEARCH & DEVELOPMENT

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The Realized Excess TDS – that measured in the mesocosms

	PreDosing					Dosing				PostDose	
Date:	19-Jul	26-Jul	28-Jul	2-Aug	9-Aug	23-Aug	6-Sep	Dosing Period	Target	20-Sep	4-Oct
Sample ID	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	Average		mg/L	mg/L
E01	226	137	182	304	266	247	236	247	240	266	
E04	178	198	262	440	413	392	343	370	361	207	
E05	263	205	420	652	NA	586	703	590	501	242	
E06	268	224	631	796	732	774	778	742	695	302	
E03	254	218	1025	1363	1337	1322	1394	1288	1062	262	
E07	277	367	1883	2273	2181	2389	1602	2066	1812	222	
E02	272	195	3100	3810	3354	3595	4214	3615	3173	480	
E08	295	65	5714	7382	7252	7130	7337	6963	5655	229	
QC_200	284		300			286	235			173	
QC_6000	5767		5753			5861	5906			5893	
QC_Blank	16		75			53	2			2	

Excess TDS was:
63% Chloride
24% Sodium
9% Calcium

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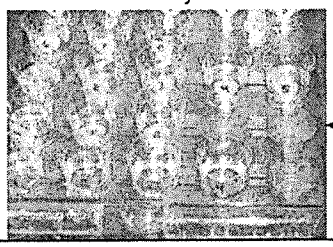
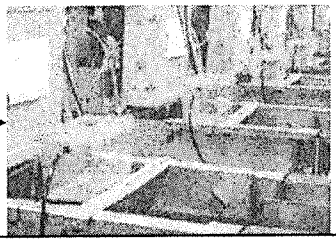
Mesocosm TDS Toxicity Tests

- Based on EPA's Acute and Chronic Whole Effluent Toxicity Manual.
- Acute tests were run simultaneously with three species. *C. triangulifer*, *Ceriodaphnia dubia*, and *Daphnia magna*
- Moderately Hard Reconstituted Water (EPA Acute Manual 2002) was used as control and dilution water.
- Chronic Tests were run on the bench top and ex-situ; 7, 14, or 20 day
- Conductivity, pH, dissolved oxygen, and temperature were recorded daily for concentrations and renewal solution.





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Chronic Test Conditions

C. dubia (based on conditions listed in EPA chronic manual)

7 days duration

Food: 0.2 ml *Selenastrum* and 0.1 ml FFAY daily
Volume: 15ml
Temperature: 25°C

Endpoint: # of young reproduced
Test Criteria: Avg. 15 young/female in 3 broods
>80% survival in control

Larval Fathead Minnow 7-day Survival/ Growth
(Modified conditions EPA chronic manual & Continuous Ex Situ Exposures)

7 days duration

Food: 0.3 ml Brine Shrimp daily/Replicate (0.3/Gallon Tank Flow Thru)
Water Volume: 250ml/Replicate
Temperature: 25°C (Temperature 20-22)

Endpoint: Growth as weight
Test Criteria: > 250 ug Mean dry weight Controls,
>80% survival in the control

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Results

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Culture Results
Generational Survival and Mortality for C. triangulifer

	Initial	Early nymph stage			Emerging nymph Stage		Adult Survival Stage	
	# of nymphs added	# of mortality	% mortality	# of mortality	% mortality	# of adult survival	% Adult survival
F3	157	3	1.91%	7	4.46%	147	93.60%
F4	150	101	67.30%	0	0.00%	49	32.70%
F5	153	2	1.31%	0	0.00%	151	98.70%
F6	159	6	3.77%	0	0.00%	153	96.20%
F7	150	108	72.00%	2	1.33%	40	26.67%
F8	103	0	0.00%	1	0.97%	102	99.03%
F9	111	0	0.00%	16	14.41%	95	85.59%

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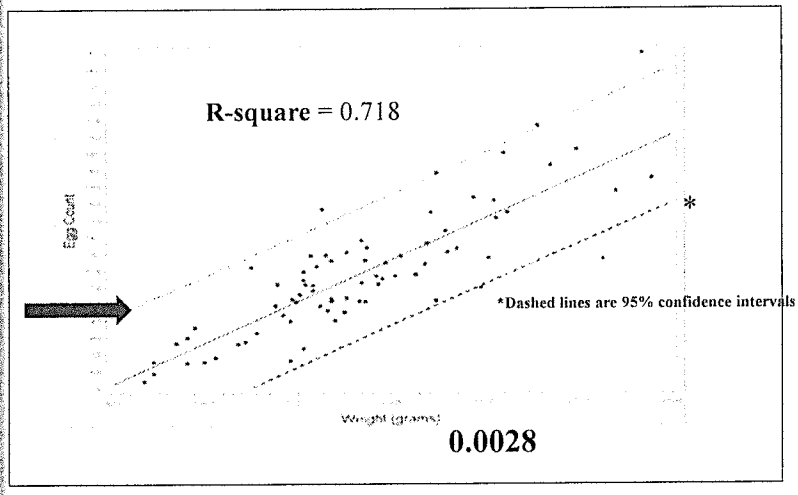
Regression Relationship Between pre Egg Laying Weight and Fecundity



Red Line indicates weight of adults at which 1000 eggs or greater will be produced

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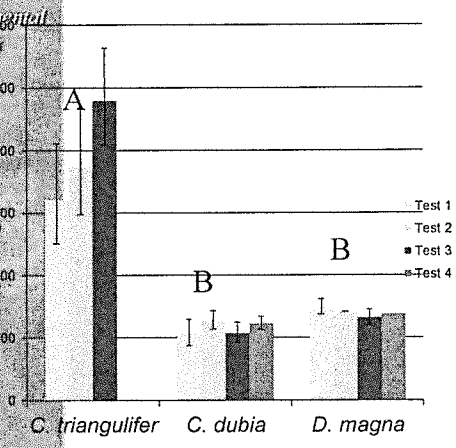
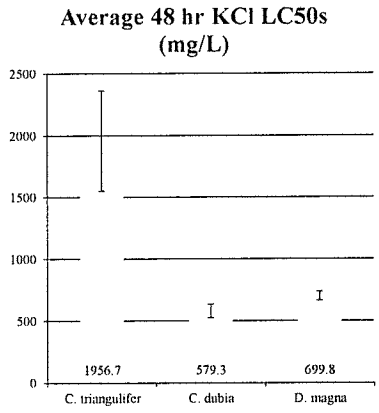
KCL Acute Results





ANOVA results indicate that *C. triangulifer* LC50s are statistically different from both *C. dubia* and *D. magna* LC50s. *C. dubia* LC50s and *D. magna* LC50s are statistically different from *C. triangulifer* but not each other.

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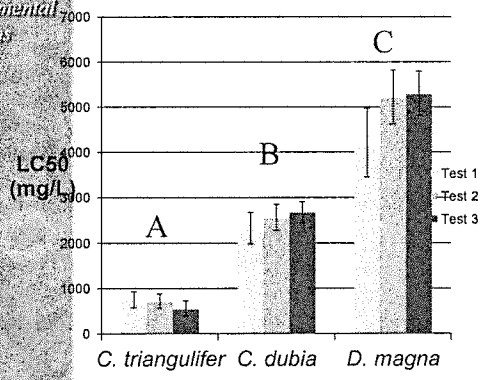
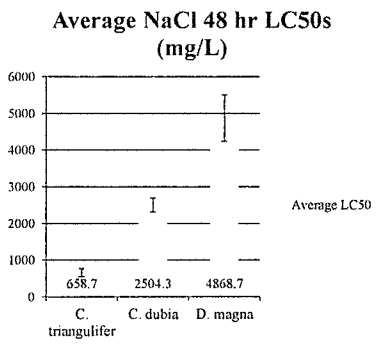
NaCl Acute Results





ANOVA results indicate that *C. triangulifer* LC50s are statistically different from both *C. dubia* and *D. magna* LC50s. *C. dubia* LC50s are statistically different from *C. triangulifer* and *D. magna*. *D. magna* LC50s are statistically different from *C. triangulifer* and *C. dubia*.

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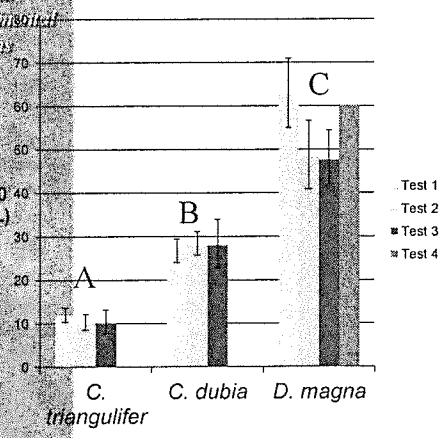
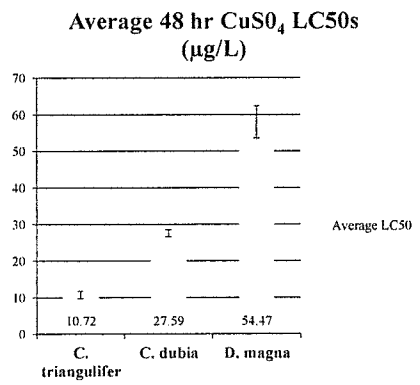
CuS04 Acute Results





ANOVA results indicate that *C. triangulifer* LC50s are statistically different from both *C. dubia* and *D. magna* LC50s. *C. dubia* LC50s are statistically different from *C. triangulifer* and *D. magna*. *D. magna* LC50s are statistically different from *C. triangulifer* and *C. dubia*.

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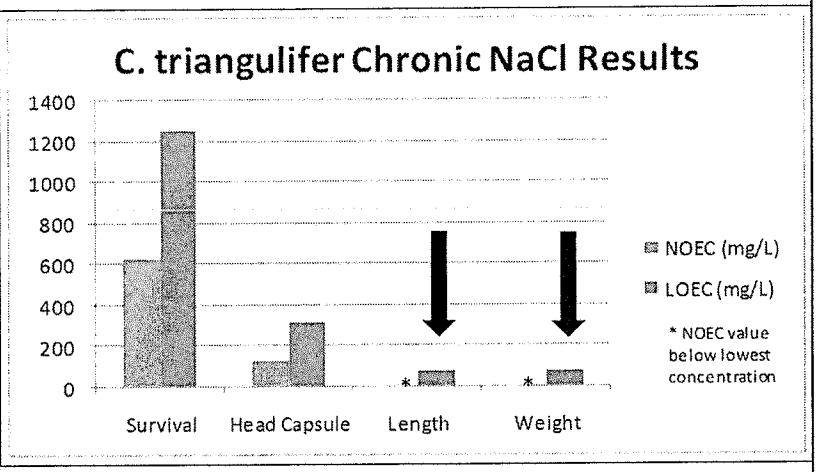
NaCl Chronic Results



Results show length and weight are more sensitive test criteria than survival and head capsule width during chronic tests.

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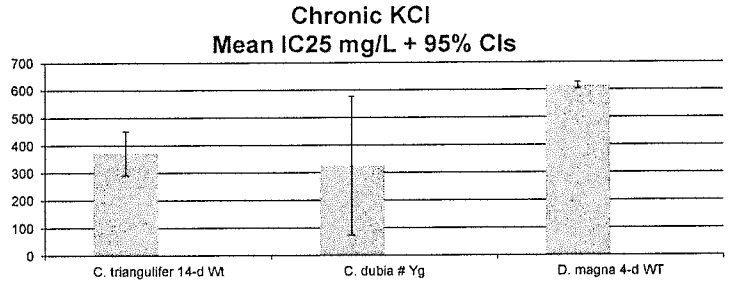
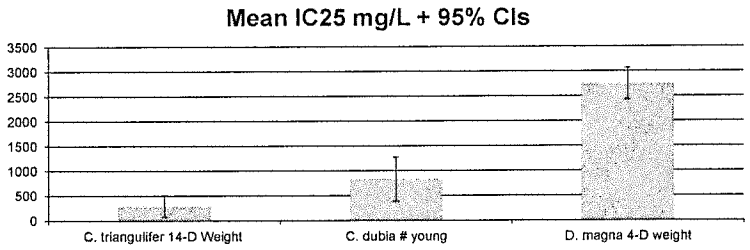
Chronic Results





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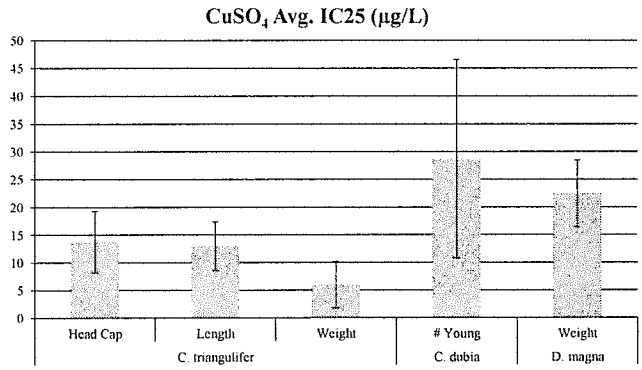
Chronic Results



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Acute Tests Results on Early Test TDS Samples in Distilled Water (DI) and East Fork River Water (EFR)

NaCl/CaCl in DI

Conc.	TDS mg/L
MHRW	nd
#1	nd
#2	242
#3	383
#4	571
#5	946
#6	1696
#7	3009
#8	5540

C. triangulifer

LC50	2720.24
95% UC	3173.55
95% LC	2331.68
NOEC	1696

C. dubia

LC50	3418.64
95% UC	3859.5
95% LC	3028.14
NOEC	1696

D magna

LC50	NA
NOEC	NA

NaCl/CaCl in EFR

Conc.	TDS mg/L
MHRW	nd
#1	nd
#2	242
#3	383
#4	571
#5	946
#6	1696
#7	3009
#8	5540

LC50	3754
95% UC	5364
95% LC	2626
NOEC	1696

LC50	3222
95% UC	3668
95% LC	2830
NOEC	1696

LC50	NA
NOEC	NA

Raw data - RESEARCH & DEVELOPMENT

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Chronic Tests Results on Samples Collected From ESF in a WET Format (3 samples collected over 7-days)

** Note, referenced constituent effect concentrations not normalized to average measured TDS, conductance, or specific ions (all nominal) at this point.*

C. triangulifer
14-day Growth Wt

Cond	IC25	977.038
	95% UC	1018.636
	95% LC	627.104
	NOEC	888
	LOEC	1268

C. dubia
7-day Fecundity

Test 1

Cond	IC25	3037.438
	95% UC	3569.509
	95% LC	895.077
	NOEC	3313
	LOEC	5116

Test 2

Cond	IC25	3895.922
	95% UC	4204.643
	95% LC	3432.734
	NOEC	3297
	LOEC	5614

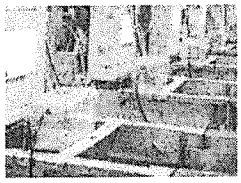
Ex Situ ESF Continuous Flow Test – 20day Duration – Chronic Results

Growth - Length

Cond	IC25	1103
	95% UC	908
	95% LC	1026
	NOEC	Control
	LOEC	567

Wing Pad Development

Cond	IC25	688
	95% UC	763
	95% LC	631
	NOEC	Control
	LOEC	567



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Chronic Tests – Growth Results 7-day Larval Fathead Minnow From ESF

WET Test 1

Cond	IC25	3727.55
	95% UC	4002.48
	95% LC	3327.72
	NOEC	
	LOEC	708

Ca	IC25	195.73
	95% UC	221.32
	95% LC	168.78
	NOEC	
	LOEC	12

Na	IC25	522.15
	95% UC	582.55
	95% LC	444.66
	NOEC	
	LOEC	32

WET Test 2

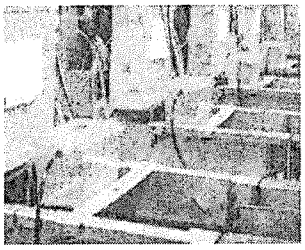
Cond	IC25	632.8
	95% UC	10859.95
	95% LC	520.58
	NOEC	
	LOEC	649

Ca	IC25	11.35
	95% UC	581.48
	95% LC	6.67
	NOEC	
	LOEC	12

Na	IC25	30.6
	95% UC	1562.45
	95% LC	19.82
	NOEC	
	LOEC	32

Ex Situ ESF Continuous Flow Test

Cond	IC25	**4036.84**
	95% UC	8076.43
	95% LC	3350.58
	NOEC	5380
	LOEC	8800



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Discussion

Culture:

- EPA-ORD Cincinnati has successfully developed a defined culture method using known species of diatoms.
- A survival rate >80% and a fecundity of 1000 eggs was achieved for five of seven generations.
- The regression relationship between pre egg laying weight adults and fecundity was significant.
- Regression analysis determined that a pre egg laying wet weight of >.00280g would give a 1000 egg count with a 95% confidence interval.

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Discussion

Toxicity Comparisons

KCl

•In 48 hr tests, *C. triangulifer* was **less** sensitive to KCl than *C. dubia* and *D. magna*

In Chronic Tests *C. triangulifer* was **as** sensitive as *C. dubia*

NaCl/CuSO4

•In 48 hr tests, *C. triangulifer* was over 2x **more** sensitive to NaCl and CuS04 than *C. dubia* and *D. magna.*

•In Chronic NaCl tests, *C. triangulifer* was 2.8X **more** sensitive than *C. dubia*

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Conclusions For Mesocom TDS Study

- Mayfly overall more sensitive to TDS than Ceriodaphnia and Larval fish.
- Larval Fathead results indicate larval fish may be as sensitive or close to *Ceriodaphnia* sensitivity.
- Organic Material and/or Suspended Solids may have slight influence on toxicity of salts.

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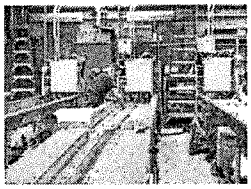
Future Research

***C. triangulifer* Testing:**

- Total Dissolved Solids (TDS) from EPA's Experimental Stream Mesocosm Study – Bench scale and in situ testing of 3 different concentrations of Marcellus Shale TDS and Coal Mine Drainage TDS

Field Experiments

- Deployments at Mountain Top Valley Fill Sites



- **Evaluating the potential for developing a representative test species indigenous to Co & Wy *Centroptilum bifurcatum* and *conturbatum* and *Drunella* (any species) – One issue maybe colder water species than *C. triangulifer*.**

Whole effluent toxicity (WET) / Alternative testing procedure (ATP) Meeting

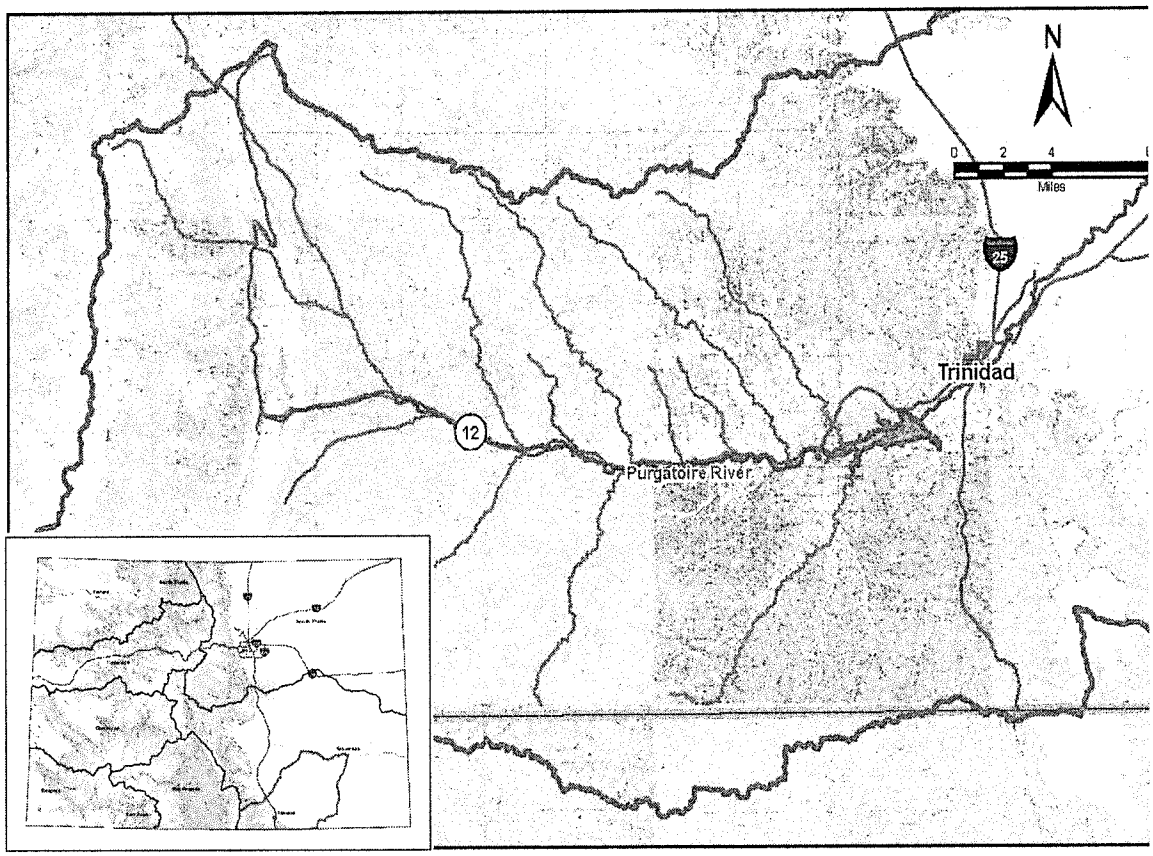
Raton Basin Watershed

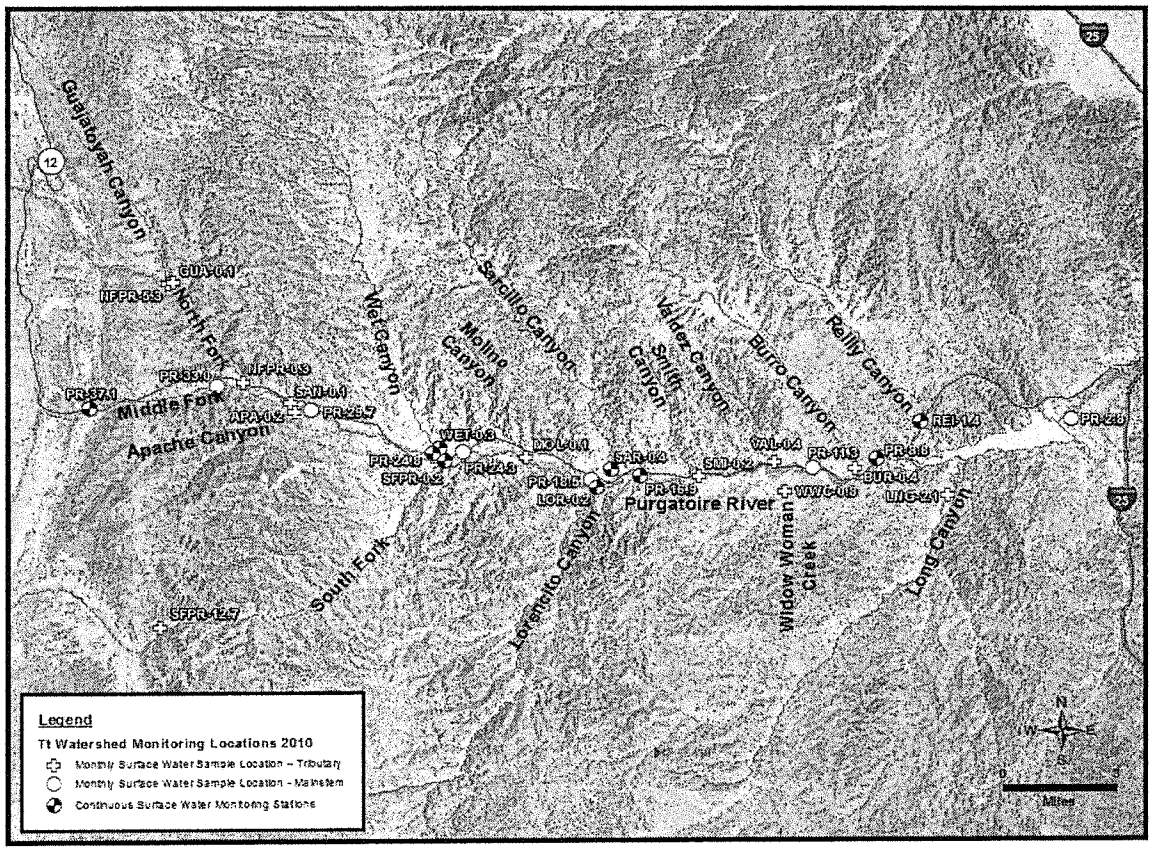
(PNR & XTO)

Objective

- Investigate the opportunity to substitute short-term chronic WET test organism (invertebrate *Ceriodaphnia dubia*) with an alternative test organism / method for testing in the Raton Basin Watershed while still being protective of aquatic species

Overview of Coal Bed Natural Gas processes in Raton Basin

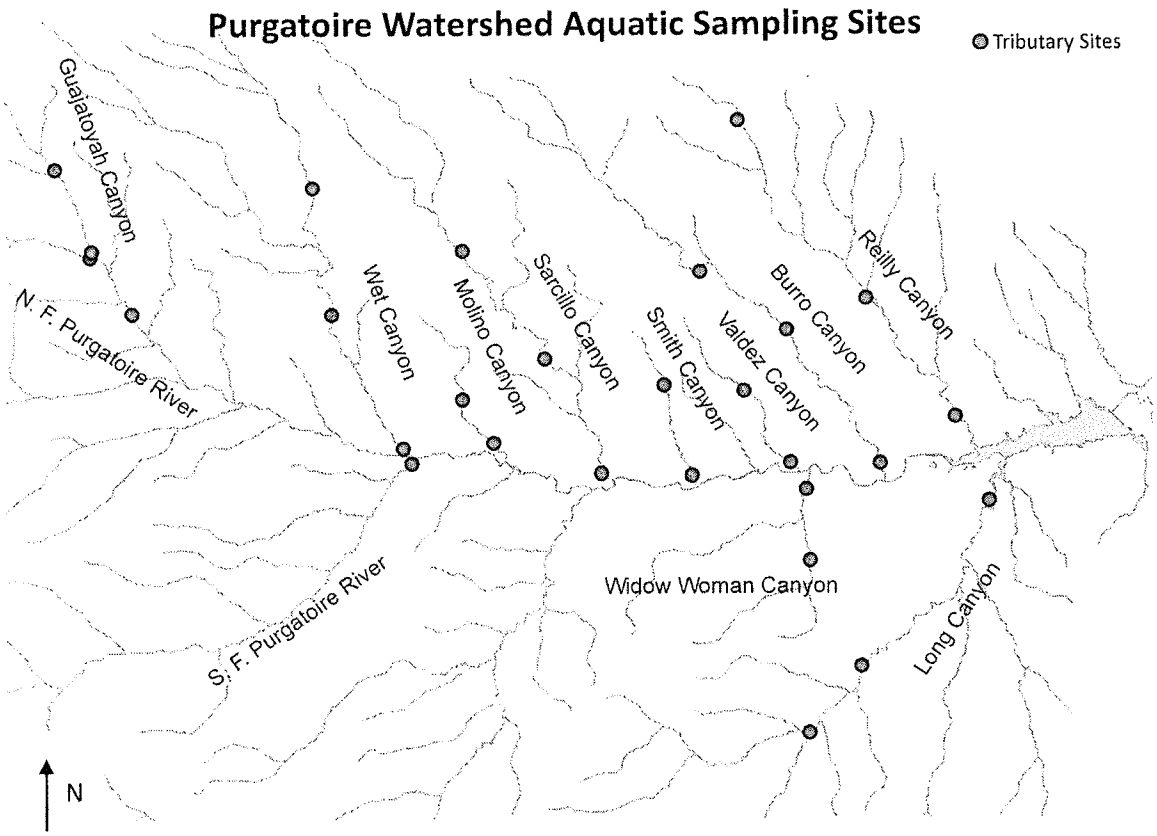


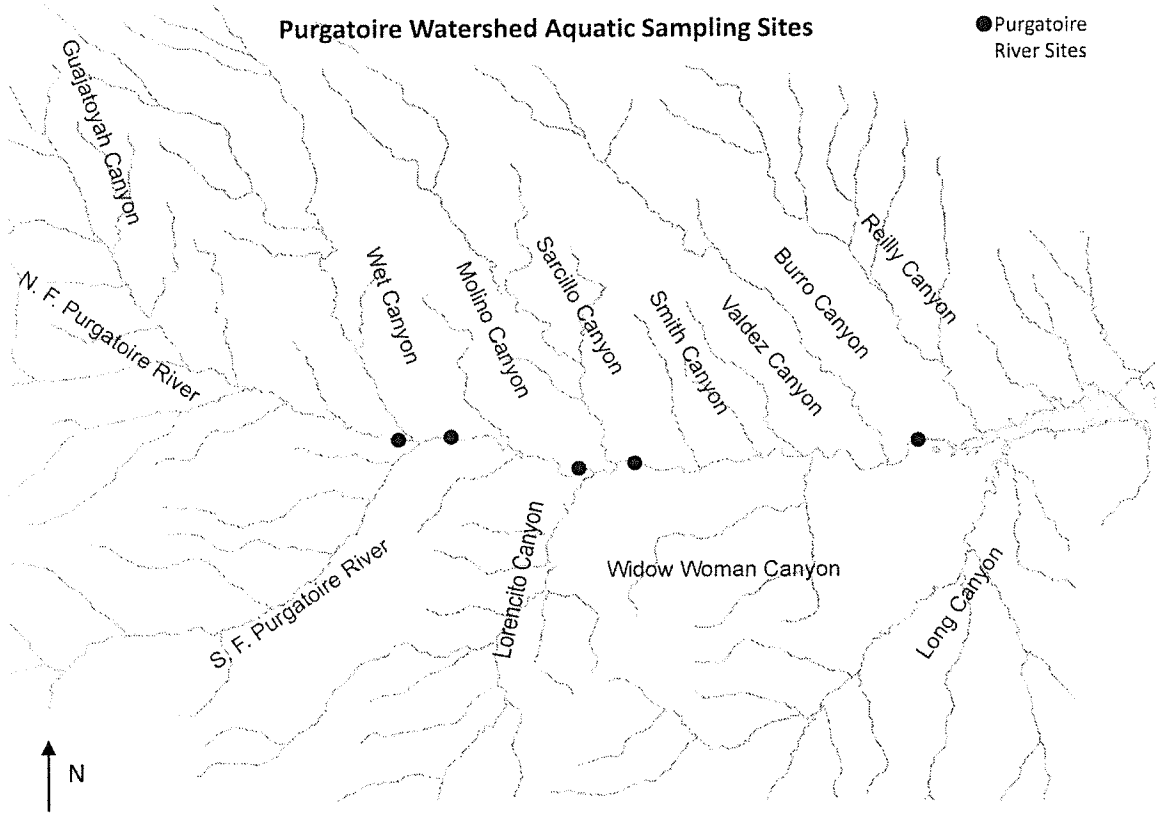


Monthly Monitoring Analyte List

Analyte Group	Constituent	Method Number	Sample Preservation and Treatment	Holding Times
Field Parameters	pH	EPA 150.1	Measure In-Situ	Immediately
	Specific Conductance	EPA 120.1		28 days
	Temperature	EPA 170.1		Immediately
Metals	Boron[D,T]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
	Calcium[D]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
	Copper[D, PD, TR]	EPA 200.8 ICP-MS	Acidify with HNO_3; pH <2	6 months
	Iron[D, TR]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
	Lead[D, PD, TR]	EPA 200.8 ICP-MS	Acidify with HNO_3; pH <2	6 months
	Magnesium[D]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
	Potassium[D]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
	Selenium[D, PD, TR]	EPA 200.8 ICP-MS	Acidify with HNO_3; pH <2	6 months
	Sodium[D]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
	Zinc[D, PD, TR]	EPA 200.7 ICP	Acidify with HNO_3; pH <2	6 months
Wet Chemistry	Alkalinity	SM2320B - Titration	Chill to 4 degrees C	14 days
	Chloride	SM4500Cl-E	Chill to 4 degrees C	28 days
	Sulfate	EPA 375.4 - Turbidimetric	Chill to 4 degrees C	28 days
	Total Suspended Solids (TSS)	SM2540D	Chill to 4 degrees C	7 days
	Total Dissolved Solids (TDS)	SM2540C	Chill to 4 degrees C	7 days

Notes:
D = Dissolved form.
PD = Potentially dissolved form.
TR = Total recoverable form.
T = Total form.
EPA = U.S. Environmental Protection Agency
SM = Standard Methods (AWWA)


Purgatoire Watershed Aquatic Sampling Sites
Tributary Sites
Guajatoyah Canyon
N. F. Purgatoire River
Wet Canyon
Molino Canyon
Sarcillo Canyon
Smith Canyon
Valdez Canyon
Burro Canyon
Reilly Canyon
Widow Woman Canyon
Long Canyon
S. F. Purgatoire River
N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Long Canyon
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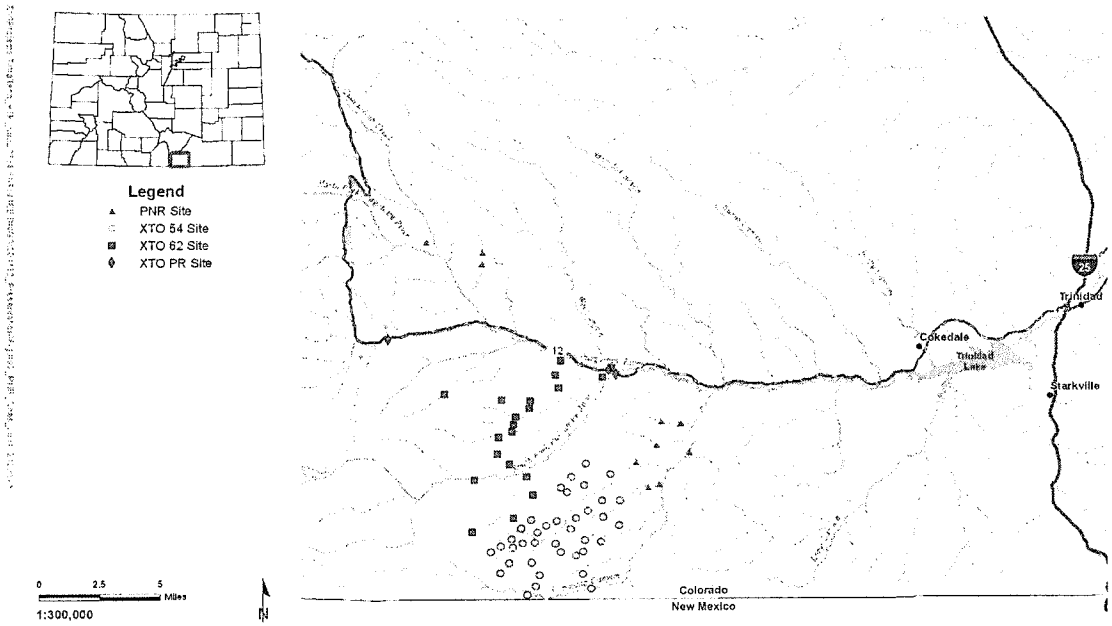
N

XTO & PNR Outfalls with chronic WET



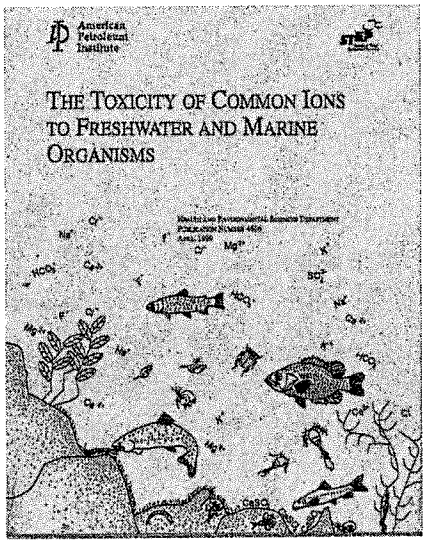
Working Hypothesis

- The toxicity observed in WET tests with *C. dubia* in this watershed is related to total dissolved solids (TDS)

- Question: Given that *C. dubia* are known to be sensitive to TDS ions would another test species (e.g., *Daphnia magna*) be a suitable replacement species in this watershed and still be protective of other aquatic species?

Total dissolved solids

- TDS toxicity in freshwaters
  - Must look at the individual ion concentrations
- Freshwater: 7 major ions
  - Cations
    - Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}
  - Anions
    - Cl^{-}, HCO_3^{-}, SO_4^{2-}
- Sources of information
  - API publication (at right)
  - GRI FW STR model
  - Goodfellow et al. 2000 *Environ Toxicol Chem*



Freshwater test organisms

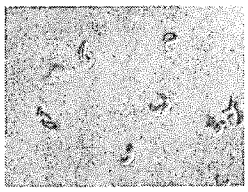
L to R
Daphnia magna
D. pulex
Ceriodaphnia dubia

Fathead minnow larvae
(*Pimephales promelas*)

Fresh water WET methods

- Acute methods (24-96-hrs)
  - Monitor lethal effects to effluents
    - Invertebrates (*C. dubia*, *D. pulex*, *D. magna*)
    - Vertebrate (*P. promelas*, *O. mykiss*)

- Short term chronic (STC) methods (4-8 d)
  - Monitor lethal and sublethal effects to effluents
    - Invertebrate
      - *C. dubia* 3-brood survival and reproduction study
    - Vertebrate
      - 7-d *P. promelas* survival and growth study
    - Plant
      - 96-h algal growth study
        - » *Pseudokirchneriella subcapitata* (at right)



Comparison of Invertebrate STC Methods

3-brood *C. dubia* test

- Duration: 6-8 days
- Organisms per chamber: 1
- Volume: 15 ml
- Reps: 10
- Temp: 25°C
- Food: 0.2 ml 1:1 algae & YCT
  - Algae (10^6 cells/ml)
- Criteria: >80% survival, 15 avg yng, 60% of cntrls must have 3 broods, PMSD (13-48)
- Endpts: survival and repro

USEPA 2002

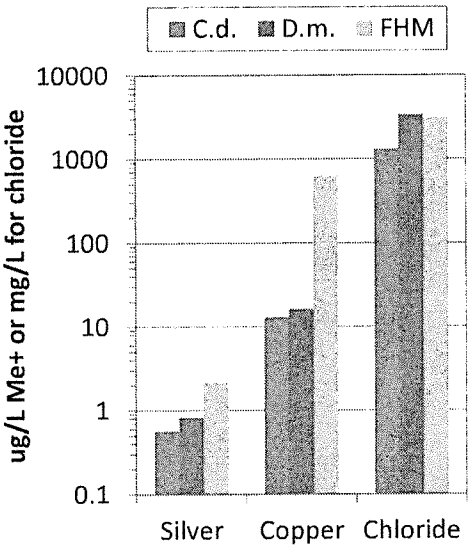
4-d *D. magna* test

- Duration: 4 days
- Organisms per chamber: 5
- Volume: 50 ml
- Reps: 4
- Temp: 25°C
- Food: 0.5 ml 3:2 algae &WG (C)
  - Algae (10^8 cells/ml)
- Criteria: >90% survival, 10X growth from pre wts
- Endpts: survival and dwt

Lazorchak et al. 2009

Relative acute sensitivity of FW species

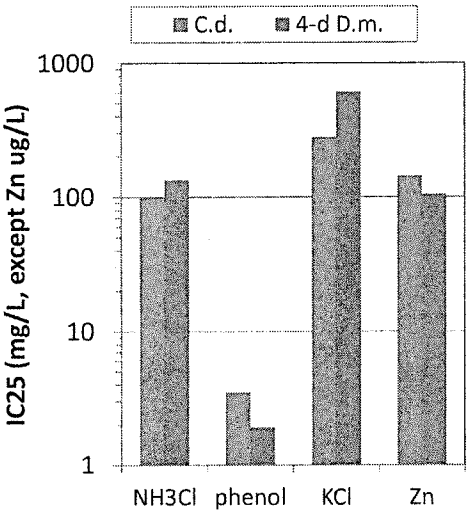
- *C. dubia*
  - one of most common aquatic test organisms
  - sensitive
- *D. magna*
  - relatively sensitive
  - tolerant of TDS ions
  - no promulgated STC mtd (chronic is 21 d)
- FHMs
  - standard aquatic vertebrate test species
  - less sensitive than inverts
    - exceptions include NH_3, sulfide



Data from AECOM

Comparison STC toxicity of methods

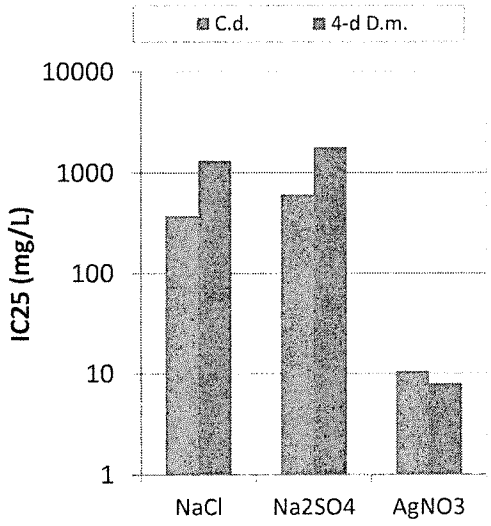
- Lazorchak et al. 2009
- Studies performed to compare STC toxicity of different toxicants using two methods
  - *C. dubia* STC
  - *D. magna* (4-d)
- Similar sensitivity of methods



Data from Lazorchak et al. 2009

Relative short-term chronic toxicity

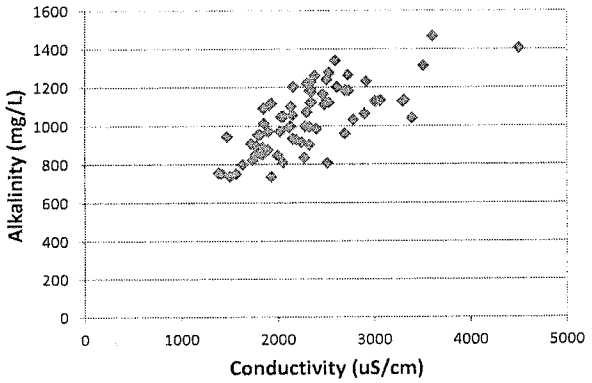
- Studies were performed to compare STC toxicity
  - *C. dubia*
  - *D. magna* (4-d)
- *D. magna* more tolerant of chloride and sulfate than *C. dubia*
- Relative anion toxicity to *C. dubia*
  - $Cl^- > HCO_3^- > SO_4^{2-}$
- Similar sensitivity to Ag



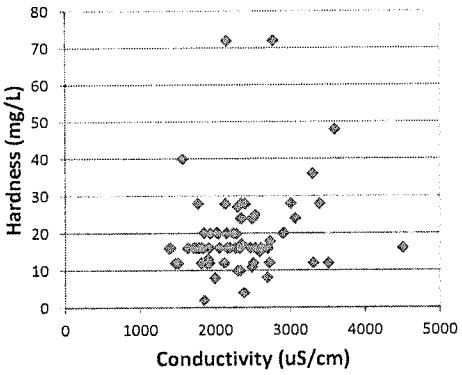
Data from AECOM

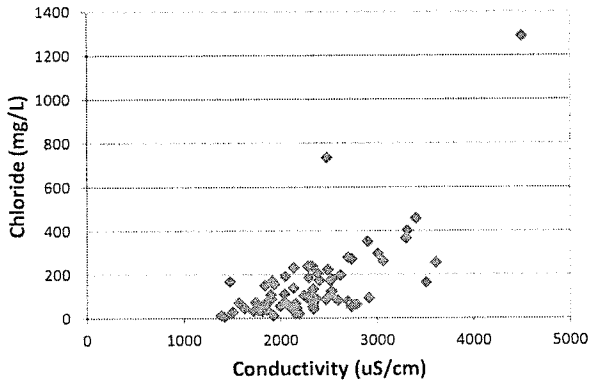
4-d *D. magna* method

- 4-d *D. magna* method shows promise as additional / alternative / site-specific test method
  - used in research / TIE studies
  - sensitivity / applicability of method
  - surrogate for *C. dubia* with TDS issues
    - Substitute in certain specific cases?



Example of relationships of different water quality Parameters in Raton Basin





ATP Work Plan outline

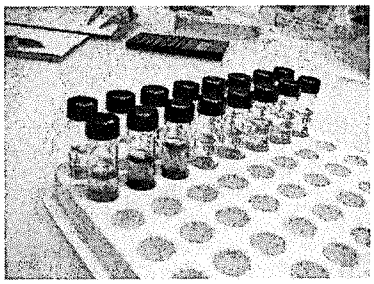
- Meet to discuss the work plan
- Toxicity testing
  - Chronic WET studies
  - Toxicity identification evaluation (Phase I TIE) studies
- Bioassessment Data / Surveys
- Final evaluation & mtgs

ATP Work Plan outline – cont.

- Toxicity testing
  - Chronic WET studies
    - *C. dubia*
    - Fathead minnows
    - *D. magna*
    - Currently performing these studies at outfalls

ATP Work Plan outline – cont.

- Toxicity testing
  - Investigating the cause of toxicity
  - Toxicity identification evaluation (Phase I TIE) studies



MeOH fractions – 2-L SPE elution

Toxicity Identification Evaluation (TIE)

- Series of physico-chemical manipulations designed to target specific types of toxicants to determine cause of toxicity
  - Some identified toxicants
    - Ammonia
    - Total Dissolved Solids (TDS) / Ions
    - OP Pesticides (Diazinon)
    - Carbamate pesticides (Carbaryl)
    - Zinc
    - Copper
    - Surfactants
    - Combination of two or more

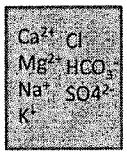
Phase I TIE Test
Baseline Toxicity (unaltered effluent)
pH Adjustment (acidic, neutral, basic)
Aeration (acidic, neutral, basic)
Filtration (acidic, neutral, basic)
Solid-phase extraction (SPE) (acidic, neutral, basic)
EDTA Chelation
Oxidant Reduction (STS)
pH Control (testing under CO_2 blanket)

Phase I TIE Manipulations

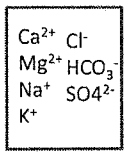
Phase I TIE Test	Toxicants Addressed	Examples
Baseline Toxicity	None (a comparison for other tests)	---
pH Adjustment	Toxicants that degrade under acidic or basic conditions	acidic = cyanide and sulfide basic = malathion
Aeration	Toxicants that are oxidizable, volatile, or sublatable	Surfactants, organic compounds
Filtration	Filterable toxicants	cationic metals under basic conditions
SPE (solid-phase extraction with C_{18})	Non-polar organic toxicants	Pesticides, VOC
EDTA Chelation	Some cationic metals	Copper, zinc, nickel
Oxidant Reduction	Oxidants, some cationic metals	Chlorine, peroxide; Copper, cadmium
Graduated pH	pH-sensitive toxicants	Ammonia, many metals, bicarbonate

ATP Work Plan outline – cont.

- Toxicity testing
  - Investigating the cause of toxicity
  - Toxicity identification evaluation (Phase I TIE) studies
    - TDS ion mock studies (Phase III TIE)
      - Match specific ion concentrations in the effluent & perform side-by-side studies (effluent & lab water)



Effluent



TDS Mock (reconstituted lab water)

ATP Work Plan outline – cont.

- Bioassessment Data / Surveys
  - Benthic macroinvertebrate surveys
  - Fish surveys
  - Periphyton surveys
  - Work performed in 2010-2011 by GEI

ATP Work Plan outline

- Would like to received input / feedback on proposed work plan
  - Additional data needs?
  - Prepare work plan
    - Submit work plan for consideration