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Evaluation of Organic Contaminants Found in Materials used for Well Construction

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Background

EPA Report from 2012

"*The Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report* (December 2012), EPA 601/R-12/011 (Appendix A)"

EPA associated a correlation between certain organics and hydraulic fracturing fluids.

glycols	phenols
benzoic acid	2-butoxyethanol

Background

It follows then that the detection of these compounds in groundwater was a result of the use of hydraulic fracturing fluids.

Or does it? What about the materials used for well construction? Are any of the compounds associated with hydraulic fracturing fluids present due to the use of certain construction materials?

Background

Bert Smith with EnviroClean Products and Services (a Chesapeake Energy contractor) organized a collaborative study to evaluate well construction materials, what organic compounds might be present and could they leach out.

Collaborators

Dr. Donald Siegel – Syracuse University
Dr. Charlie Carter – TestAmerica Laboratories, Inc.
Chuck Neslund – Eurofins Lancaster Laboratories Environmental, LLC.

Study

Steps of the Study to be Evaluated

1. What well construction materials should be considered?
2. Are any of the organics identified by the EPA reasonably expected to be present in well construction materials?
3. Can we confirm/determine the presence of these compounds in the well construction materials?
4. For those compounds determined in the well construction materials, do they leach out from the "deployed" material?

Construction Materials

Many different kinds of materials used in well construction but based on amount used, frequency of use and potential for impact on groundwater we selected;

- Portland Cement Type I/II
- Bentonite

Compound List

Resulting from an internet search, literature search and reference to the following document;

Ervanne and Hakanen, *Analysis of Cement Superplasticizers and Grinding Aids, A Literature Survey,* Working Report 2007-15; April, 2007 (page 29)

We learned that glycols, glycol ethers, phenols, alkanolamines and alcohols are all used as grinding aids and are common cement additives.

Compound List

The group agreed to use analytical techniques that were well accepted for the analysis of constituents. Since there was not a good consistent analytical technique for the alkanolamines, that class of compounds was not considered for the study.

Compound List

Compound	Method
Ethylene Glycol	SW-846 8321 (LC/MS/MS)
Propylene Glycol	SW-846 8321 (LC/MS/MS)
Diethylene Glycol	SW-846 8321 (LC/MS/MS)
Triethylene Glycol	SW-846 8321 (LC/MS/MS)
Tetraethylene Glycol	SW-846 8321 (LC/MS/MS)
2-Butoxyethanol	SW-846 8321/SW-846 8270C
Ethanol	SW-846 8260B
Isopropanol	SW-846 8260B
n-Propanol	SW-846 8260B
tert-Butyl alcohol	SW-846 8260B
Acetone	SW-846 8260B
2-Butanone (MEK)	SW-846 8260B
Phenol	SW-846 8270C
2-Methylphenol	SW-846 8270C
3/4-Methylphenol	SW-846 8270C
2,4-Dimethylphenol	SW-846 8270C
Benzoic Acid	SW-846 8270C

Compound List

To assess the presence of these compounds in Portland Cement and Bentonite products, materials were purchased from several different home-improvement retail stores in Oklahoma and New Mexico.

- 5 Portland Cement Products
  - Type I and Type I/II
- 10 Bentonite Products
  - Chips, Drilling viscosifier, % solids grout and coated/uncoated pellets

Compound List

Materials were given generic designations and were subsampled and sent to each laboratory.

A duplicate of one of each type of material was randomly chosen and also submitted to each laboratory.

Laboratories coordinated on mixing ratios for each of the products.

i.e. all cement mixed in 1:1 ratio with water, bentonite ratios varied based on product

Results – SW-846 8321

Compound	Testing Lab	Cement A ug/kg	Cement B ug/kg	Cement C ug/kg	Cement D ug/kg	Cement E ug/kg	Cement F (Duplicate of A) ug/kg	Container and Trip Blank ug/kg	Method Blanks ug/kg
Ethylene Glycol	TA	7500J	<1100	<5400	<1100	2800J	8900J	<27	<27
	LAN	5500	<500	1000	<500	1600	8000	<500	<500
Propylene Glycol	TA	<900	<180	<900	<180	<450	<900	<4.5	<4.5
	LAN	<100	<100	<100	130	110	<100	<100	<100
Diethylene Glycol	TA	37000	<150	33000	<150	14000	37000	3.7J	<3.7
	LAN	34000	50	31000	230	10000	28000	<25	<25
Triethylene Glycol	TA	79000	<120	5200	<120	20000	76000	<3.1	<3.1
	LAN	71000	<25	4200	<25	20000	66000	<25	<25
Tetraethylene Glycol	TA	11000	<80	<400	<80	2500	11000	<2.0	<2.0
	LAN	9400	<25	360	<25	2300	9800	<25	<25
2-butoxyethanol	TA	33J	<12	<12	<12	51J	<12	<12	<12
	LAN	12	<5	<5	<5	36	13	<5	<5

Results – SW-846 8260B

Compound	Testing Lab	Cement A ug/kg	Cement B ug/kg	Cement C ug/kg	Cement D ug/kg	Cement E ug/kg	Cement F (Duplicate of A) ug/kg	Container and Trip Blank ug/kg	Method Blanks ug/kg
Ethanol	TA	<94	<94	<94	<94	<94	<94	<94	<94
	LAN	<2500	<2500	<2500	<2500	<5000	<2500	<250	<250
Isopropanol	TA	17JB	18JB	15JB	<13	<13	<13	35JB	38.4J
	LAN	<1000	<1000	<1000	<1000	<1000	<1000	<100	<100
n-propanol	TA	DJ	DJ	DJ	DJ	DJ	DJ	ND	DJ
	LAN	ND	ND	ND	ND	ND	ND	ND	---
tert-butyl Alcohol	TA	<11	<11	<11	<11	<11	<11	<11	<50
	LAN	<800	<800	<800	<800	<1600	<800	<80	<80
Acetone	TA	19	73	70	77	62	58	57	<1.9
	LAN	<200	<200	<200	<200	<400	<200	<20	<20
2-Butanone	TA	5.7J	7.6	6.1	3.2J	4.5J	2.7J	7.4	<2.0
	LAN	<100	<100	<100	<100	<200	<100	<10	<10

Results – SW-846 8270C

Compound	Testing Lab	Cement A ug/kg	Cement B ug/kg	Cement C ug/kg	Cement D ug/kg	Cement E ug/kg	Cement F (Duplicate of A) ug/kg	Container and Trip Blank ug/kg	Method Blanks ug/kg
Phenol	TA	<0.35	56	140	210	<0.44	<0.43	<0.42	<0.34
	LAN	<1	29	71	120	<1	<1	<1	<1
2-Methylphenol	TA	<0.42	<0.51	<0.52	<0.53	<0.53	<0.51	<0.50	<0.41
	LAN	<1	<1	<1	<1	<1	<1	<1	<1
3&4-Methylphenol	TA	<0.64	<0.79	<0.79	<0.81	<0.80	<0.77	<0.76	<0.63
	LAN	<1	<1	<1	<1	<1	<1	<1	<1
2,4-Dimehtylphenol	TA	<0.47	<0.57	<0.58	<0.59	<0.58	<0.56	<0.55	<0.45
	LAN	<1	<1	<1	<1	<1	<1	<1	<1
Benzoic Acid	TA	61	18J	<2.1	<2.1	<2.1	74	<2.0	<1.6
	LAN	17	<16	19	22	19	18	<15	<15

Results Summary

Results between the two laboratories were reasonably similar.

The alcohols and other volatiles were not detected so will not be carried into leaching evaluation.

Because they were consistently detected by both labs the glycols, 2-butoxyethanol, benzoic acid and phenol would be carried through to next phase.

Leachability

Two aspects of leachability to be investigated

Phase 1 – Short Term Exposure of Cured Cement.

Cured cement exposed to laboratory water for 24 hours. Water removed, clean water added and exposed for another 24 hours. Repeated for 5 days

Phase 2 – Long Term Exposure of Cured Cement

Four similar quantities of cured cement exposed to laboratory water for 1, 5, 10 and 20 days.

Leachability

Leachability

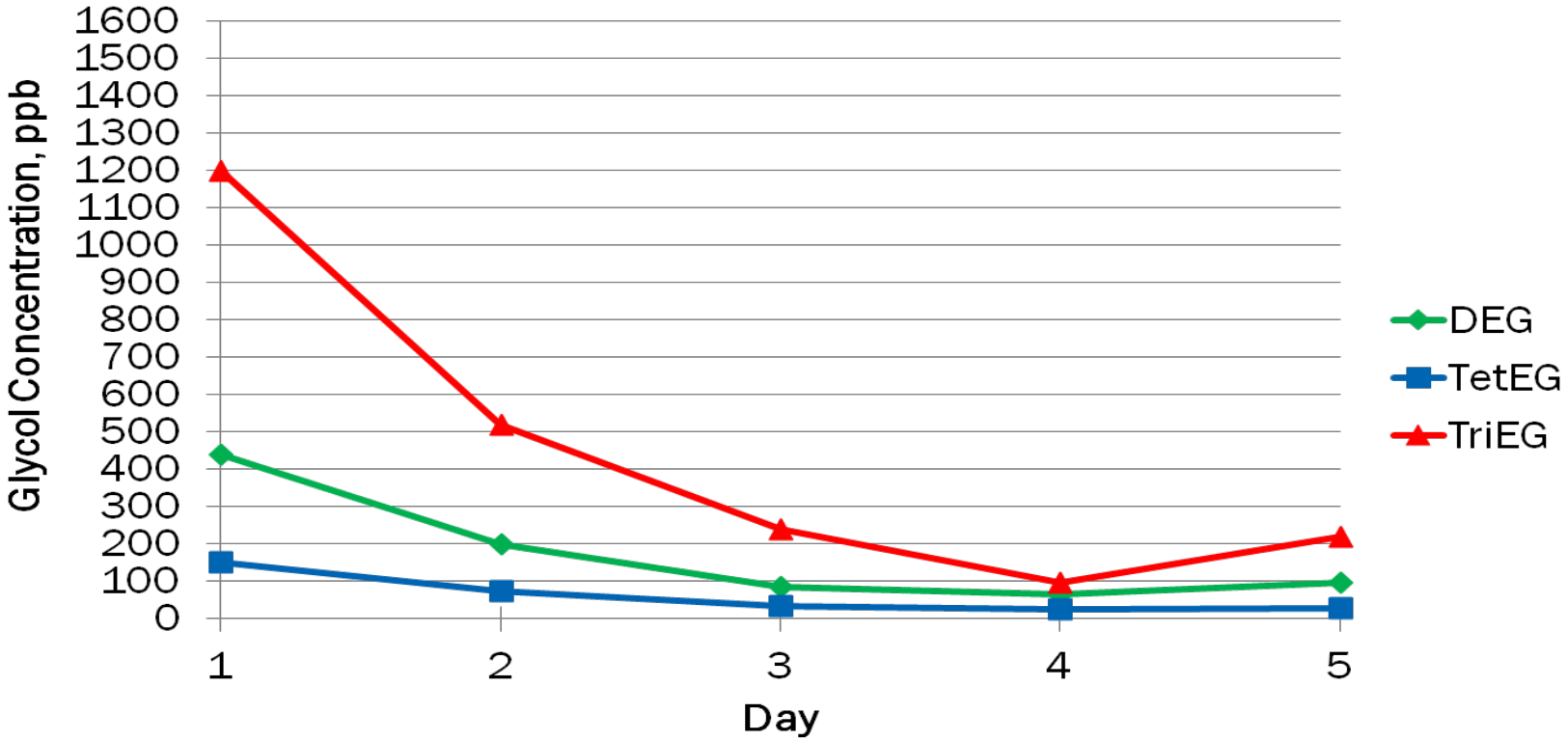
Phase 1

Phase 2

Leachability – Phase 1 Results

Compound	Testing Lab	Day 1	Duplicate (Day 1)	Day 2	Day 3	Day 4	Day 5	Method Blank(s)
Ethylene Glycol	TA	<540	<540	<270	<540	<540	<270	<27
	LAN	<500	<500	<500	<500	<500	<500	<500
Propylene Glycol	TA	<90	<90	<45	<90	<90	<45	<4.5
	LAN	<100	<100	<100	<100	<100	<100	<100
Diethylene Glycol	TA	540	230	170	110	88	78	<3.7
	LAN	440	550	200	85	66	97	<25
Triethylene Glycol	TA	1500	1400	580	400	300	250	<3.1
	LAN	1200	1000	520	240	95	220	<25
Tetraethylene Glycol	TA	160J	190	95	78	62	52	<2.0
	LAN	150	130	74	34	<25	28	<25
2-butoxyethanol	TA	<12	<12	<12	<12	<12	<12	<1.5
	LAN	<5	<5	<5	<5	<5	<5	<5
Benzoic Acid	TA	14J	15J	14J	14J	18J	15J	<1.5
	LAN	<16	<16	<16	<15	<15	<15	<15
Phenol	TA	<0.33	<0.33	<0.33	<0.33	<0.33	<0.34	<0.32
	LAN	<1	<1	<1	<1	<1	<1	<1

Leachability – Phase 1 Results



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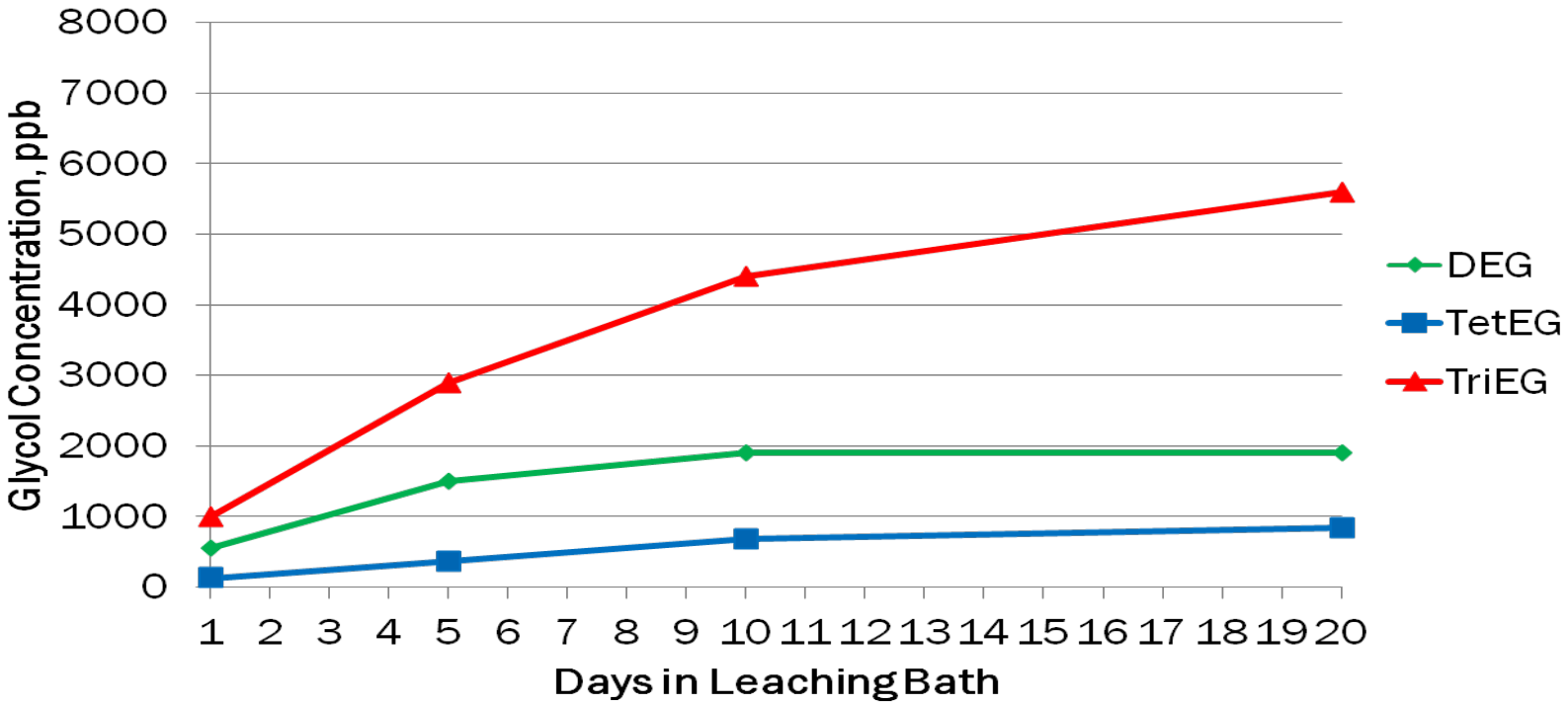
Leachability – Phase 2 Results

Compound	Testing Lab	Day 1	Duplicate (Day 1)	Day 5	Day 10	Day 20	Method Blanks (3)
Ethylene Glycol	TA	<540	<540	<540	<1400	<1400	All <27
	LAN	<500	<500	<500	<500	560	All <500
Propylene Glycol	TA	<90	<90	<90	<230	<230	All <4.5
	LAN	<100	<100	<100	<100	<100	All <100
Diethylene Glycol	TA	230	540	1200	1800	2200	All <3.7
	LAN	550	440	1500	1900	1900	All <25
Triethylene Glycol	TA	1400	1500	4200	6100	7100	All <3.1
	LAN	1000	1200	2900	4400	5600	All <25
Tetraethylene Glycol	TA	190	160J	630	730J	900J	All <2.0
	LAN	130	150	360	680	840	All <25
2-butoxyethanol	TA	<12	<12	<12	<12	<12	All <12
	LAN	<5	<5	<5	<5	<5	All <5
Benzoic Acid	TA	15J	14J	15J	5.8J	7.5J	All <1.5
	LAN	<16	<16	<16	<15	<15	All <15
Phenol	TA	<0.33	<0.33	<0.33	<0.34	<0.36	All <0.32
	LAN	<1	<1	<1	<1	<1	All <1

Leachability – Phase 2 Results



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Conclusions

- Several of the compounds potentially associated with hydraulic fracturing fluids are found in well construction materials
- Glycols were detected at substantial concentrations
- The use of 8321 allows for the determination of glycol concentrations not previously possible with 8015
- The compounds detected in cement do leach in water from the cured product under short term and long term exposure scenarios

Acknowledgements

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