Evaluation of Potential Impacts of Hydraulic Fracturing Flowback Fluid Additives on Microbial Processes in Publicly-Owned Treatment Works (POTWs)

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Gradient

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List of Abbreviations

BOD	Biochemical Oxygen Demand
dSGEIS	Draft Supplemental Generic Environmental Impact Statement
HESI	Halliburton Energy Services, Inc.
HF	Hydraulic Fracturing
HQ	Hazard Quotient
MGD	Million Gallons Per Day
NYSDEC	New York State Department of Environmental Conservation
PA	Pennsylvania
POTW	Publicly-owned Treatment Works
QSAR	Quantitative Structure-Activity Relationship
RBC	Risk-Based Concentration
SPDES	State Pollutant Discharge Elimination System
TSS	Total Suspended Solids
WV	West Virginia

1 Introduction

The New York State Department of Environmental Conservation (NYSDEC) published a Draft Supplemental Generic Environmental Impact Statement (dSGEIS), dated September 2009, which contains generic permit requirements for the development of natural gas production wells in the Marcellus Shale formation using horizontal drilling and high-volume hydraulic fracturing techniques (NYSDEC, 2009). This memorandum evaluates potential risks of upsetting microbial processes in a wastewater treatment plant from exposure to typical additives likely to be present in hydraulic fracturing (HF) flowback fluid. Gradient has prepared this report on behalf of Halliburton Energy Services, Inc. (HESI).

2 Hydraulic Fracturing Flowback Fluid Disposal to a POTW

Several options exist or are being developed for treatment, recycling or reuse of flowback water generated during HF operations.[1] One option is treatment of flowback water at publicly-owned treatment works (POTWs), which typically discharge effluent to surface waters, and are regulated in New York State by the State Pollutant Discharge Elimination System, commonly referred to as SPDES. The POTW's permit defines whether it can accept non-domestic waste and includes specific discharge limitations and monitoring requirements. A POTW must have a State-approved "pretreatment" program in order to accept industrial wastewater (such as HF flowback water). POTWs must also notify NYSDEC of any new industrial waste or of substantial changes in the volume or character of pollutants they plan to receive at their facility. NYSDEC must then determine if the SPDES permit needs to be modified.

In addition to an approved pretreatment program, a headworks analysis is required for a POTW to be able to accept HF flowback water. The data required for conducting a headworks analysis are specified in the dSGEIS (pp. 7-58 and 7-59) and include: general chemistry and aquatic toxicity. The POTW will utilize these data to determine whether the volumes and concentrations of chemicals present in the HF flowback water can be accepted by the facility and the changes needed to the facility's permit. One of the key objectives of a headworks analysis is to determine whether HF additives could adversely affect the POTW's microorganisms resulting in disruption of the POTW operation and diminished effluent quality. Therefore, this report presents such an analysis to predict the likely impact of HF additives in flowback water, if any, on microorganisms at a POTW.

[1] Information summarized in Section 2 of this memo is based upon information presented in the dSGEIS (NYSDEC, 2009).

3 Assessment of Potential Impacts of Hydraulic Fracturing Flowback Fluid Additives on POTW Biological Processes

Typically, microorganisms are used in the secondary treatment of wastewater to decompose organic matter at a POTW. As such, conditions in this secondary (biological) wastewater treatment step need to be conducive to microorganism survival. Failure to meet such conditions can cause an upset of the wastewater treatment process and can result in effluents that are not sufficiently treated for discharge to surface water.

3.1 Exposure Analysis

As discussed in Section 2, POTWs operate under permitting programs to ensure that upset conditions and discharges of inadequately treated wastewater are avoided under typical conditions. To evaluate the risk of flowback fluid from Marcellus Shale hydraulic fracturing operations causing disruption of POTW biological treatment processes, we used typical HF operations described in the dSGEIS, and operational information provided by HESI to Gradient, and assessed the potential impacts on POTW microorganisms for the operating conditions listed in Table 1.

Table 1
HF Flowback Disposal to a POTW – Operational Assumptions

POTW Treatment	
HF Disposal (gal/truck)	5,000
Transportation Rate (trucks/day)	10
Disposal Rate (gal/day)	50,000
POTW Flow (gal/day)	2,000,000[a]
Flowback Fluid Dilution in POTW (disposal rate/POTW flow)	40

Notes:
[a] Median POTW design flow for POTWs listed in Appendix 21 of the dSGEIS.

Based on the list of POTWs permitted to accept industrial wastewater listed in the dSGEIS, the median POTW flow capacity among these POTWs is 2 million gallons per day (MGD) (see Appendix 21 dSGEIS). It is anticipated that a typical HF flowback disposal rate could be 50,000 gal/day, resulting in a 40-fold dilution of the HF flowback fluid with other influent water. To calculate exposure concentrations to which microorganisms in a typical wastewater treatment plant would be exposed, the 40-fold dilution factor was applied to:

- Maximum selected representative pollutant concentrations for the model HF fluid listed in Table 6.13 of the dSGEIS (dSGEIS model HF fluid); and
- Maximum measured flowback constituent concentrations,[2] based on limited data from Pennsylvania and West Virginia listed in Table 6.2, dSGEIS.[3]

POTW microorganism exposure concentrations for the dSGEIS model HF fluid are presented in Table 2 and exposure concentrations for the flowback fluid based on PA and WV data are presented in Table 3. These exposure concentrations were compared to microbial toxicity effect concentrations to characterize potential risks for disruption of biological treatment processes at a typical POTW.

3.2 Effects Analysis

Traditionally, municipal wastes have been mineralized biologically, employing an assortment of microorganisms. These wastes normally contain readily biodegradable organic substances, however with rapid industrialization, certain synthetic organic chemicals have been shown to cause upset conditions and POTW permit violations. Microbial toxicity data for synthetic organic chemicals are limited. Nonetheless, measured toxicity data were found for three (3) out of the 13 chemicals listed in the dSGEIS HF model fluid (Table 2), and all four (4) synthetic organic chemicals measured in flowback fluid from PA and WV (Table 3). The lowest median inhibitory concentration (IC50),[4] reported in Trevizo and Nirmalakhandan (1999) or Nirmalakhandan *et al.* (1994), to have an effect on activated sludge, methanogens, nitrobacteria, or two commercial cultures (Polytox and Microtox) was used as the effects concentration [Risk-Based Concentration (RBC)] for POTW microorganisms.

With advances in quantitative structure-activity relationships (QSARs) it has become increasingly possible to derive models using available test results that can reliably predict toxicity for chemicals lacking effects data. For example, aqueous solubility was shown to be a reliable predictor of microbial toxicity by Trevizo and Nirmalakhandan (1999). These authors demonstrated statistically significant correlations between experimental toxicity data [(log (IC50)] and experimental water solubility data [log (solubility)]. An overall correlation was found to be:

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[2] Constituent concentration estimates based on ≤ 3 measurements were not considered sufficiently robust and were not further retained in our analysis.

[3] As stated in the dSGEIS, characteristics of flowback fluid from the Marcellus shale in New York are expected to be similar to flowback from PA and WV, but not identical (NYSDEC, 2009).

[4] IC50 (the median inhibitory concentration): This is a measure of the effectiveness of a chemical in inhibiting biological or biochemical function. For instance, in the Microtox assay, it is the concentration of a chemical at which 50% reduction in bioluminescence by marine bacteria occurs.

log (IC50, mM/l) = 0.68 log (Solubility, mM/l) - 0.25

with a correlation coefficient of 0.756 for nearly 200 data points. This correlation was used to predict microbial toxicity values (RBC) for the remaining organic chemicals in the dSGEIS model HF fluid.

3.3 Risk Characterization

The risk characterization for our analysis is presented as an HQ, or hazard quotient, relating the estimated HF flowback constituent concentrations in a typical POTW to the chemical's risk-based concentration, or RBC:

$$HQ = \frac{POTW\ Conc}{RBC}$$

The numerator of this equation (POTW Conc) was calculated using the dSGEIS HF model fluid or measured flowback data (from PA and WV) and applying a dilution factor of 40. The denominator of this equation is the risk-based concentrations that were derived in the previous section. An HQ value of less than 1 indicates that adverse effects on POTW microorganisms are unlikely.

Since all predicted HQs are substantially lower than 1 (Table 2), none of the synthetic organic constituents in the dSGEIS model HF fluid are present at concentrations that are expected to adversely impact biological treatment processes at a typical POTW. Similarly, measured concentrations in HF flowback fluid from PA and WV, after dilution at a typical POTW are more than 3 orders of magnitude below microbial effect concentrations and are therefore not expected to upset plant treatment processes (Table 3).

There are a number of additional constituents listed in Table 3, such as conventional pollutant parameters [*e.g.*, biochemical oxygen demand (BOD), pH, total suspended solids (TSS), oil & grease, *etc.*] and non-conventional parameters (*e.g.*, metals). These additional constituents are commonly treated at POTWs and regulated under the SPDES permitting program to ensure compliance with applicable statutory and regulatory requirements. Therefore, these parameters are not expected to cause microbial toxicity and disrupt biological treatment processes under the conditions specified in a typical POTW facility's permit.

4 Conclusion

We evaluated potential risks of upsetting microbial processes in a wastewater treatment plant from exposure to typical organic additives likely to be present in Marcellus Shale HF flowback fluid. Our analysis demonstrates that organic additives in the dSGEIS HF model fluid and measured flowback fluid data from PA/WV are not expected to cause microbial toxicity and upset conditions at POTWs that would treat such discharges in New York. Conventional (*e.g.*, BOD, pH, TSS, oil & grease, *etc.*) and non-conventional pollutants (*e.g.*, metals) present in HF flowback fluid are commonly treated at POTWs and regulated under the SPDES permitting program to ensure compliance with applicable statutory and regulatory requirements using pre-treatment approaches. They are therefore not expected to cause microbial toxicity and disrupt biological treatment processes under the conditions specified in the POTW's permit. Based on the analysis presented herein, it can be concluded that the organic HF fluid additives listed in the dSGEIS (both in the dSGEIS HF model fluid and in measured flowback data) are present at concentrations substantially below those that might result in disruption of biological treatment processes at typical POTWs treating HF flowback fluids in New York and therefore the possibility that these HF fluid additives might cause an upset condition is *de minimis*.

References

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Table 2
HF Flowback Disposal
Acute Risks to Microorganisms Based on Model dSGEIS Fluid Concentrations

Chemical	CasNo	Purpose	Flowback Conc (ug/L)[1]	POTW Conc (ug/L)[2]	Water Solubility (ug/L)[3]	RBC (ug/L)[4]	Source[5]	HQ[6]
Acrylamide	79-06-1	Friction Reducer	10,000	250	640,000,000	19,532,667	M	1.28E-05
Benzene	71-43-2	Corrosion Inhibitor	0.01	0.00025	2,000,000	74,986	E	3.33E-09
Diammonium Peroxidisulphate	7727-54-0	Breaker	100,000	2,500	559,000,000	25,876,231	M	9.66E-05
Ethylene Glycol	107-21-1	Crosslinker/Breaker/Scale Inhibitor	180,000	4,500	1,000,000,000	25,335,072	M	1.78E-04
Formaldehyde	50-00-0	Corrosion Inhibitor	500	13	400,000,000	10,770,069	M	1.16E-06
Glutaraldehyde	111-30-8	Biocide	90,000	2,250	709,980,000	23,389,127	M	9.62E-05
Hydrochloric Acid	7647-01-0	Acid	385,000	9,625	720,000,000	2,467,612	M	3.90E-03
Methanol	67-56-1	Surfactant/Cross Linker/Scale Inhibitor	984,000	24,600	1,000,000,000	20,000,000	E	1.23E-03
Monoethanolamine	141-43-5	Crosslinker/Corrosion Inhibitor	18,000	450	1,000,000,000	25,205,057	M	1.79E-05
Heavy Naphtha	64742-48-9	Gelling Agent	275,000	406	406	1,439	M	2.82E-01
Propargyl Alcohol	107-19-7	Corrosion Inhibitor	1,500	38	1,000,000,000	24,522,739	M	1.53E-06
Propylene Glycol	57-55-6	Breaker, Surfactant	500,000	12,500	811,000,000	23,451,858	M	5.33E-04
Xylene	1330-20-7	Solvent	3,000	75	106,000	140,144	E	5.35E-04

Notes:
1 - Maximum concentrations in flowback taken from Table 6-13 in dSGEIS (dSGEIS, 2009)
2 - Concentration in POTW = Flowback concentration/POTW dilution factor (40)
3 - Water solubility predicted using EPA's Epi Suite Software pakcage (v 4.0)
4 - RBC = Risk-Based Concentration (IC50) from Trevizo and Nirmalakhandan, 1999 or Nirmalakhandan et al., 1994
5 - RBC Source = Modeled (M) or Experimental (E) - note, the lowest experimentally-derived RBC using either activated sludge, methanogens, nitrobacter or two commercial cultures (Polytox and Microtox) was used
6 - HQ = Hazard Quotient = POTW Conc/RBC

Table 3
HF Flowback Disposal
Acute Risks to Microorganisms Based on Measured Flowback Fluid Concentrations from PA and WV

Chemical	CasNo	Flowback Conc (ug/L)[1]	POTW Conc (ug/L)[2]	Water Solubility (ug/L)[3]	RBC (ug/L)[4]	Source[5]	HQ[6]
Phenols[7]	64743-03-9	440	11	8,470	17,881	E	6.15E-04
Toluene	108-88-3	3,190	80	526,000	207,000	E	3.85E-04
Benzene	71-43-2	1,950	49	2,000,000	74,900	E	6.51E-04
Ethyl Benzene	100-41-4	164	4.1	169,000	129,515	E	3.17E-05
Xylenes	1330-20-7	2,670	67	106,000	140,144	E	4.76E-04
Bromide	24959-67-9	3,070,000	76,750	NE	NE	NA	NE
Nickel	7440-02-0	137	3.4	NE	NE	NA	NE
Iron	7439-89-6	810,000	20,250	NE	NE	NA	NE
Lithium	7439-93-2	161,000	4,025	NE	NE	NA	NE
Magnesium	7439-95-4	3,190,000	79,750	NE	NE	NA	NE
Manganese	7439-96-5	14,500	363	NE	NE	NA	NE
Aqueous ammonia	7664-41-7	382,000	9,550	NE	NE	NA	NE
Sodium	7440-23-5	96,700,000	2,417,500	NE	NE	NA	NE
Potassium	7440-09-7	7,810,000	195,250	NE	NE	NA	NE
Strontium	7440-24-6	5,841,000	146,025	NE	NE	NA	NE
Copper	7440-50-8	157	3.9	NE	NE	NA	NE
Zinc	7440-66-6	90	2.3	NE	NE	NA	NE
Barium	7440-39-3	15,700,000	392,500	NE	NE	NA	NE
Boron	7440-42-8	26,800	670	NE	NE	NA	NE
Cadmium	7440-43-9	1,200	30	NE	NE	NA	NE
Calcium	7440-70-2	34,000,000	850,000	NE	NE	NA	NE
Cobalt	7440-48-4	580	14.50	NE	NE	NA	NE
Sulfate	14808-79-8	1,270,000	31,750	NE	NE	NA	NE
Alkalinity, Carbonate, as CaCO3	NA	117,000	2,925	NE	NE	NA	NE
Oil and Grease	NA	1,470,000	36,750	NE	NE	NA	NE
Total Organic Carbon	NA	1,080,000	27,000	NE	NE	NA	NE
Bicarbonates	NA	1,708,000	42,700	NE	NE	NA	NE
pH	NA	8.0	NA	NE	NE	NA	NE
Chloride	NA	228,000,000	5,700,000	NE	NE	NA	NE
Total Dissolved Solids	NA	337,000,000	8,425,000	NE	NE	NA	NE
Total Kjeldahl Nitrogen	NA	585,000	14,625	NE	NE	NA	NE
Chemical Oxygen Demand	NA	31,900,000	797,500	NE	NE	NA	NE
Total Suspended Solids	NA	1,910,000	47,750	NE	NE	NA	NE
Biochemical Oxygen Demand	NA	4,450,000	111,250	NE	NE	NA	NE

Notes:
1 - Maximum measured concentrations taken from Table 6-2 in dSGEIS (dSGEIS, 2009)
2 - Concentration in POTW = Flowback concentration/POTW dilution factor (40)
3 - Water solubility predicted using EPA's Epi Suite Software pakcage (v 4.0)
4 - RBC = Risk-based concentration (IC50) from Trevizo and Nirmalakhandan, 1999 or Nirmalakhandan et al., 1994
5 - RBC Source = Experimental (E) - note, the lowest experimentally-derived toxicity value using either activated sludge, methanogens, nitrobacter or two commercial cultures (Polytox and Microtox) was used
6 - HQ = Hazard Quotient = POTW Conc/RBC
7 - Phenol (CAS 108-95-2) was used as a surrogate
NA - Not Applicable
NE - Not Evaluated