

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

Prepared for

Halliburton Energy Services, Inc.
P.O. Box 42806
Houston, TX 77242-2806

January 10, 2012



Gradient

www.gradientcorp.com

Science and Strategies for Safe Environments

20 University Road
Cambridge, MA 02138
617-395-5000

Table of Contents

	<u>Page</u>
1	Introduction 1
2	Hydraulic Fracturing Flowback Fluid Disposal to a POTW 3
2.1	HF Process 3
2.2	Regulatory Requirements 3
3	Potential Impacts of Flowback Constituents on POTW Treatment 5
3.1	Flowback Dilution in POTWs 6
3.2	Flowback Constituent Concentration Estimation 8
3.3	Microorganism Toxicity Benchmarks 14
3.4	Risk Characterization..... 15
4	Conclusion 18
5	References 19

List of Tables

Table 1	Flowback Disposal to a POTW – Range of DAF Values
Table 2	Flowback Fluid Organic Constituents and Hazard Quotients
Table 3	Typical HESI Hydraulic Fracturing Fluid Systems
Table 4	Organic Constituents in Typical HESI HF Fluid Systems and Hazard Quotients
Table 5	POTW Microorganism Hazard Indices for Typical HESI HF Fluid Systems

Abbreviations

BOD	Biochemical Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
dSGEIS	2009 Draft Supplemental Generic Environmental Impact Statement
revised dSGEIS	2011 Revised Draft Supplemental Generic Environmental Impact Statement
HESI	Halliburton Energy Services, Inc.
HF	Hydraulic Fracturing
HQ	Hazard Quotient
HI	Hazard Index
MGD	Million Gallons Per Day
NPDES	National Pollutant Discharge Elimination System
NYSDEC	New York State Department of Environmental Conservation
POTW	Publicly-owned Treatment Works
QSAR	Quantitative Structure-Activity Relationship
RBC	Risk-Based Concentration
SPDES	State Pollutant Discharge Elimination System
TDS	Total Dissolved Solids
TSS	Total Suspended Solids

1 Introduction

The New York State Department of Environmental Conservation (NYSDEC) published a Revised Draft Supplemental Generic Environmental Impact Statement (revised dSGEIS), dated September 2011 (NYSDEC, 2011). The revised dSGEIS has been updated based on public comment and further analysis by NYSDEC since it released the prior draft SGEIS (dSGEIS) in September 2009 (NYSDEC, 2009). The revised dSGEIS 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 (HF) techniques (NYSDEC, 2011).

This report, which was prepared on behalf of Halliburton Energy Services, Inc. (HESI), evaluates the potential for flowback water recovered from the HF process in the Marcellus Shale to upset the treatment process at a Publicly Owned Treatment Works (POTW). As discussed further in Section 3, our analysis focuses on the organic constituents that may be found in flowback due to their use in HF fluids, as well as certain organic constituents that have been measured in flowback samples and that occur naturally in the Marcellus Shale. We do not focus on inorganics and conventional wastewater parameters because such parameters have been routinely treated in POTWs for decades, and are commonly subject to effluent discharge limits (which may in turn possibly require pretreatment in certain cases to achieve the discharge limits) in order to ensure that these parameters will not upset treatment processes.

Section 2 of this report provides an overview of flowback fluid recovery and disposal considerations, including an overview of applicable regulations on flowback disposal. Section 3 describes the methodology used to evaluate potential impacts of flowback on wastewater treatment at POTWs, with a specific emphasis on biological treatment processes. The methodology consists of three central components:

1. Estimation of potential concentrations of constituents in flowback water – and particularly the organic constituents that are the focus of this study – and their respective concentrations when mixed in the overall flow of wastewater being treated at a POTW;
2. Determination of "risk-based concentrations" (RBCs) for these constituents in flowback that reflect the potential for a constituent to adversely affect the biological treatment stage in POTW systems; and
3. Calculation of "Hazard Quotients," which represent the ratio of the predicted flowback constituent concentrations at a POTW to their associated risk-based concentrations, to assess whether the flowback constituent concentrations could exceed the RBCs and thereby potentially lead to POTW treatment upset conditions.

As summarized in the concluding Section 4, our results indicate that treatment of the organic constituents in flowback water from HF activities at POTWs is not expected to upset biological wastewater treatment processes at these facilities. All of the Hazard Quotients are less than 1 (*i.e.*, $HQ < 1$), indicating that flowback constituent concentrations in POTWs are expected to be less than their respective RBCs. The RBCs are based on toxicity values from published studies where available, and estimated from Quantitative Structure Activity Relationships (QSARs) when measured values were not readily available. The use of QSARs to estimate chemical toxicity (and by extension RBCs) is an approach that is routinely adopted by the U.S. Environmental Protection Agency (US EPA). For example, the US EPA Office of Pollution Prevention and Toxics (OPPT) has developed its ECOSAR (Ecological Structure Activity Relationship) model to fill data gaps where little or no experimental measured data exists.¹

In addition, we also conservatively estimated the cumulative impact of HF constituents that could be present in flowback by summing all of the Hazard Quotients for the constituents of various HF fluid systems to estimate Hazard Indices for the different fluid systems. Similarly, all of the Hazard Indices are less than 1 (*i.e.*, $HI < 1$) for these fluid systems. As discussed more fully in this report, the conservative approaches adopted here lend a high level of confidence that flowback from HF activities, and particularly the organic constituents that are the focus of this study, will not disrupt POTW treatment processes. The results of this analysis indicate that the appropriateness of routine detailed headworks analyses proposed in the revised dSGEIS should be reconsidered with respect to organic constituents in flowback – our analysis indicates little likelihood for these constituents to upset POTW treatment processes.

¹ <http://www.epa.gov/oppt/newchemicals/tools/ecosartechfinal.pdf>

2 Hydraulic Fracturing Flowback Fluid Disposal to a POTW

This section provides a brief overview of the HF process, flowback fluid recovery, and regulatory considerations for flowback disposal.

2.1 HF Process

As described more fully in the revised dSGEIS (NYSDEC, 2011), hydraulic fracturing typically involves large volumes of fluids (generally consisting mostly of water), pumped under high pressure, to fracture the target formation to allow for natural gas production. The fluids also contain chemical constituents ("HF constituents") to enhance the fracturing process; these constituents typically comprise approximately 0.5% by weight of the total amount of fluid used in the hydraulic fracturing process. Once the fracturing is complete, and the fluid pressure removed, fluids pumped into the shale formation along with naturally occurring fluids from the shale formation are recovered from the well as "flowback" fluids.

Several options exist, or are being developed, for treatment, recycling, and reuse of flowback generated during HF operations. Although there is a trend towards increasing the recycling and reuse of flowback, proper disposal is required for flowback water that is not reused. Disposal of flowback fluids is often accomplished through deep underground injection wells. In New York, disposal *via* underground injection is not expected to occur; treatment of flowback at POTWs is a potential alternative disposal option.

2.2 Regulatory Requirements

The NYSDEC utilizes an EPA-approved program for the control of wastewater effluent discharges directly to surface waters, referred to as the State Pollutant Discharge Elimination System (SPDES). SPDES permits are issued to wastewater dischargers, including Publicly-Owned Treatment Works (POTWs), who typically discharge treated effluent to surface waters. The POTW's permit defines whether the POTW 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.²

² EPA considers flowback to be an industrial wastewater that is subject to pretreatment requirements. EPA Office of Wastewater Management, Natural Gas Drilling in the Marcellus Shale, NPDES Program Frequently Asked Questions (March 16, 2011) at 8.

Current federal Clean Water Act regulations at 40 CFR Part 435, Subpart C do not include pretreatment standards that specifically address disposal of flowback into POTWs. However, EPA's General Pretreatment regulations under the National Pollutant Discharge Elimination System (NPDES) prohibit the introduction into a POTW of wastewaters that contain pollutants which could "pass through" (*i.e.*, flow through the POTW without any treatment) or cause interference with POTW operations (US EPA, 2011). In addition, the federal regulations establish best practicable control technology (BPT) requirements for treatment of wastewater from onshore oil and gas exploration activities, and these requirements preclude direct discharge of untreated wastewater pollutants into navigable waters for produced water (*e.g.*, flowback) and other wastes (US EPA, 2011). Under federal NPDES regulations, and the New York SPDES regulations, POTWs must also notify the permitting agency (NYSDEC in this case) 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 to accept the wastewater. For example, NYSDEC states in the revised dSGEIS that SPDES permits for POTWs that accept flowback from Marcellus Shale operations would be modified to include influent and effluent limits for parameters such as total dissolved solids (TDS). In addition to these existing NPDES/SPDES regulations, the US EPA recently announced its intention to develop effluent guidelines for the discharge of wastewater from natural gas development from Coalbed Methane formations, and to develop pretreatment requirements for flowback from shale gas extraction.³ This draft plan calls for US EPA to collect data and information regarding flowback from shale gas extraction activities (such as those in the Marcellus Shale) and develop information on available treatment technologies. This proposed plan may ultimately lead to the development of effluent guidelines for flowback water from shale gas extraction.

As part of the revised dSGEIS, NYSDEC has proposed measures that include a headworks analysis (also known as a Maximum Allowable Headworks Loading Analysis) for a POTW to be able to accept flowback water from shale gas wells.⁴ The data required for conducting such a headworks analysis are specified in the revised dSGEIS (NYSDEC, 2011), and include defining flowback chemical composition and testing for potential aquatic toxicity. Using this information, the POTW would determine whether the volumes and concentrations of constituents present in flowback water could be accepted by the facility and whether changes might be needed to the facility's SPDES permit. One of the key objectives of the proposed headworks analysis is to determine whether HF flowback could adversely affect the POTW treatment process (particularly biological treatment) and could thereby result in disruption of the POTW

³ Federal Register, Vol. 76, No. 207, Wednesday, October 26, 2011.

⁴ POTW procedures for accepting high-volume HF wastewater are described in Appendix 22 of the revised dSGEIS (NYSDEC, 2011).

operation and diminished treatment effectiveness. This report presents a conservative screening-level assessment to evaluate whether flowback, or more specifically the organic constituents that may be associated with flowback, from HF activities in the Marcellus Shale are likely to upset the POTW treatment process.

3 Potential Impacts of Flowback Constituents on POTW Treatment

Wastewater treatment at a POTW is a multi-step process that typically includes: (i) primary treatment to remove suspended solids; (ii) secondary treatment to decompose organic matter; and (iii) sometimes tertiary treatment to remove nutrients. At facilities accepting industrial wastewater, there may also be a pretreatment step to reduce the concentration of inorganic chemicals to levels below those that might upset the secondary and tertiary treatment stages. Typically, biological treatment processes (and specifically microorganisms) are used in the secondary and tertiary (if used) wastewater treatment steps. As such, conditions in these treatment stages need to be conducive to microorganism survival. If high concentrations of certain constituents are introduced into a POTW, they could impair the survival of beneficial microorganisms, cause an upset of the wastewater treatment process, and may result in the discharge of inadequately treated POTW effluent to surface water.

This section presents the approach used to develop a potential range of flowback constituent concentrations at POTWs which may treat flowback. We evaluate a possible range of dilution of the flowback water into the overall POTW wastewater stream. Considering a range of dilution scenarios provides insight on how potential constituent concentrations at the POTW might vary under a range of possible flowback water characteristics.

Our analysis focuses on the potential for organic constituents in flowback to upset the POTW treatment process. We focus on organic constituents for several reasons. First, conventional wastewater constituents (*e.g.*, BOD, pH, TSS, oil & grease, *etc.*) and inorganic chemicals, such as metals, have been commonly treated for decades at POTWs, using pre-treatment approaches where required. Second, in addition to pretreatment (if required), mixing of flowback water with other wastewater received at a POTW for the purpose of compliance with effluent discharge limits will reduce concentrations of such constituents to levels that are not expected to have an adverse effect on microorganisms. In the Federal Register notice issued by US EPA announcing its intent to develop pretreatment requirements for flowback from shale gas extraction, US EPA acknowledged that POTWs follow this practice with flowback, blending the flowback with traditional POTW wastewater to ensure that TDS concentrations do

not cause upset conditions.⁵ NYSDEC has indicated that it expects this practice to be followed in New York, with SPDES permits for POTWs that accept flowback from shale gas wells being modified to include limits for parameters such as TDS to ensure that TDS levels will not cause upset conditions. For example, in its analysis in the revised dSGEIS of potential dilution of flowback being treated at a POTW, NYSDEC assumed that TDS concentrations in POTW effluent would be 1,000 mg/L.⁶ This TDS concentration is relatively low compared to concentrations at which adverse effects in microorganisms are exhibited. Typically, adverse effects in microorganisms that could result in upset conditions at a POTW are not expected to occur until TDS concentrations are on the order of 10,000 mg/L.⁷ Therefore, at a typical POTW, conventional and inorganic constituents are not likely to upset the POTW treatment process. Overall, given the considerable experience at POTWs with handling such conventional and inorganic constituents these constituents are not addressed in this analysis. Thus, the remaining analysis focuses on organic constituents that may be present in flowback water to be treated at POTWs.

3.1 Flowback Dilution in POTWs

In order to assess whether organic constituents in flowback water could disrupt the biological treatment processes within a POTW, it is necessary to determine the concentration of a particular constituent within the overall waste stream being treated at the POTW. When flowback water is accepted at a POTW, the concentrations of flowback constituents will be diluted in the POTW as a result of mixing within the other (*i.e.*, municipal and industrial) wastewater stream being treated at the POTW. The diluted concentration of a flowback constituent after being mixed into a POTW can be stated as:

$$C_{POTW} = \frac{C_F}{DAF} \quad (3-1)$$

where:

- C_{POTW} = Flowback chemical concentration in POTW ($\mu\text{g/L}$)
- C_F = Chemical concentration in flowback water ($\mu\text{g/L}$)
- DAF = Dilution Attenuation Factor

⁵ US EPA. "Notice of Final 2010 Effluent Guidelines Program Plan." Fed. Reg. 76(207):66296, October 26.

⁶ TDS measures the salt content of the wastewater, *i.e.*, the combination of inorganic chemicals, such as chloride, sulfate, bromide, and other constituents of salts.

⁷ Hashad M., Sharma S., Nies L., and Alleman J. 2006. "Study of Salt Wash Water Toxicity on Wastewater Treatment." Joint Transportation Research Program, Purdue University.

The revised dSGEIS estimates the anticipated dilution of flowback within POTWs. The estimate is premised on the amount of dilution required to reduce the high total dissolved solids (TDS) concentration in flowback to a concentration of 1,000 mg/L.⁸ On this basis, the revised dSGEIS indicates that a DAF of up to 500 may be needed to reduce TDS concentrations in flowback water to a concentration of 1,000 mg/L (NYSDEC, 2011, p. 6-62). This DAF is based on the highest reported TDS concentration in Marcellus flowback (350,000 mg/L), and thus represents the maximum dilution factor, or an upper-bound DAF. Using this same approach, less dilution would be needed for flowback fluid containing TDS at less than this high-end concentration. For example, applying the same methodology, but instead using the median TDS concentration in flowback of 63,800 mg/L (a more typical value) presented in the revised dSGEIS (revised dSGEIS, Table 5-10), yields a DAF of approximately 100.⁹

In our previous analysis (Gradient, 2009), we had derived a DAF of 40 for flowback treatment at a POTW. However, our understanding regarding likely operations with respect to the Marcellus Shale in New York State has evolved as more information has become available and as NYSDEC has further refined its proposed conditions for those operations during the SGEIS process. Given our current understanding of likely HF operations, we have concluded that a DAF of 40 is not realistic.¹⁰ Therefore, in this current POTW analysis we have used DAF values of 100 (median) and 500 (upper-bound) to assess a range of anticipated dilution factors when treating flowback at a POTW (Table 1). This approach is consistent with the approach adopted by NYSDEC in the revised dSGEIS.

Table 1. Flowback Disposal to a POTW – Range of DAF Values

Flowback Scenario	DAF
Median Total Dissolved Solids	100 ^[a]
Upper-Bound Total Dissolved Solids	500 ^[b]

Notes:

^[a] Derived using median TDS (63,800 mg/L) and method adopted in revised dSGEIS (p. 6-62)

^[b] Dilution Factor for maximum TDS (350,000 mg/L) presented in revised dSGEIS (p. 6-62)

⁸ This TDS limit for POTW effluent in the revised dSGEIS appears to be an assumption in NYSDEC’s analysis and not necessarily a proposed permit limit. TDS limits for POTWs are determined on a case-by-case basis and are specified in a POTW’s SPDES permit.

⁹ The DAF calculated assuming flowback at the median TDS concentration (63,800 mg/L) yields a DAF of 91, which we have rounded up to 100 for simplicity.

¹⁰ That prior estimate was based on flowback recovery rates for 8 wells per well pad. The revised dSGEIS indicates that only 4 wells would be installed in any year on a well pad, which would reduce flowback volume by half of what we had used in our 2009 study. A reduced volume of flowback would therefore be mixed in with the same volume of other wastewater at a POTW, resulting in greater dilution of the flowback. For this reason, our prior DAF of 40 is no longer relevant.

Note that for flowback with TDS concentrations below the median value reported in the revised dSGEIS, lower DAF values could be derived using the revised dSGEIS methodology. However, in our analysis, we have used the very conservative assumption that constituents are present at their maximum detected concentrations in flowback (*e.g.*, "worst-case" conditions). We applied a range of DAFs for this worst case scenario as a sensitivity analysis, by evaluating these high-end concentrations in conjunction with median and maximum DAFs. At the same time, it is highly implausible that flowback containing maximum concentrations of organic constituents would simultaneously have lower than normal levels of TDS that would lead to a low DAF. Therefore, we did not evaluate a scenario of maximum concentrations and minimum DAFs, because the coupling of two extreme (*i.e.*, overly conservative) assumptions would have created an unrealistic scenario that is not expected to occur.

3.2 Flowback Constituent Concentration Estimation

In order to assess a comprehensive range of organic constituents that could potentially be present in flowback fluids, we utilized two sources of information:

- Constituents that have been measured in flowback samples from the Marcellus Shale in Pennsylvania and West Virginia (reported in revised dSGEIS); and
- HF chemical constituents that are used in typical HESI HF fluid systems that could potentially be recovered in flowback.

The measured flowback constituents are based on samples of flowback liquids recovered from HF operations in the Marcellus Shale region of Pennsylvania and West Virginia. The constituents measured in these samples represent a combination of naturally occurring compounds from the shale formation and HF constituents that are returned with flowback after the HF stimulation. The organic constituents in flowback water from Marcellus Shale samples are summarized in the revised dSGEIS (Table 5.10). For our analysis, we have included organic flowback constituents detected in more than three (3) samples.¹¹ The maximum detected flowback constituent concentrations, which were utilized in our analysis, are summarized in Table 2.

¹¹ Constituent concentration estimates based on ≤ 3 measurements were not considered sufficiently robust and were not evaluated in our analysis.

Table 2. Organic Constituents Measured in Flowback and Hazard Quotients

Chemical	CAS Number	Det	N	Measured Flowback Concentration (ug/L) ¹	Concentration in POTW (ug/L) ²		Water Solubility (ug/L) ³	RBC (ug/L) ⁴	HQ ⁵	
					DAF = 100	DAF = 500			DAF = 100	DAF = 500
Benzene	71-43-2	14	35	1,950	20	3.9	1,790,000	74,986	3E-04	5E-05
Ethyl Benzene	100-41-4	14	38	164	1.6	0.3	169,000	129,527	1E-05	3E-06
Toluene	108-88-3	15	38	3,190	32	6.4	526,000	109,647	3E-04	6E-05
Xylenes	1330-20-7	15	22	2,670	27	5.3	106,000	140,144	2E-04	4E-05

Notes:

- 1 - Maximum measured concentrations taken from Table 5.10 in dSGEIS, 2011,
- 2 - Concentration in POTW = Flowback concentration/POTW Dilution Factor (DAF),
- 3 - Estimated water solubility from EPA's Epi Suite Software package (v 4.10),
- 4 - RBC = Risk-based concentration (IC50) from using Trevizo and Nirmalakhandan (1999) linear regression equation (see text),
- 5 - HQ = Hazard Quotient = POTW Conc/RBC

As a supplement to this dataset, we evaluated a suite of HF constituents used in typical HESI HF formulations. HESI has developed HF fluid formulations for hydraulic fracturing in the Marcellus formation, as well as other oil and gas formations in other regions of the US. Designations for a number of typical HESI HF fluid systems, as well as the typical volume of fluids used during various fracturing stages are presented in Table 3. Although only a subset of these systems are anticipated to be used in the Marcellus formation, we have evaluated all of the HF constituents that are included in these systems as a comprehensive measure.

We used the maximum concentration of HF constituents spanning all of the typical HESI HF fluid formulations (regardless of whether targeted for use in the Marcellus or not) in this assessment. Table 4 lists the typical HF chemical constituents and their maximum concentrations across all of the typical HESI HF systems.

We have assumed for purposes of this analysis that all of the constituents used in typical HESI HF fluid systems are recovered in flowback water at the same concentration as they are introduced at the wellhead. This is a very conservative assumption, and a highly unlikely scenario for several reasons. For example, HF constituents will be diluted into formation fluids, and will also likely diffuse into rock pore spaces and adsorb to the formation, some becoming trapped in pinched-off fractures beyond the continuous fracture network. Other constituents will break down in the formation (either through biodegradation or abiotic reactions). These mechanisms are expected to significantly reduce the concentrations of these constituents in flowback water. Thus, the assumption that HF constituents in flowback would be found at the same concentrations as they are introduced at the wellhead is unrealistic, and therefore adds a high degree of conservatism to our analysis. In addition, for the measured flowback constituents, we used the maximum measured concentration values in our analysis. Thus, our results represent an upper-bound screening evaluation of whether the maximum concentration of organic constituents in flowback may have the potential to upset POTW treatment processes.

Table 3 Typical HESI Hydraulic Fracturing Fluid Systems

Formulation Name	Fluid Stage Designation	Fluid Volume (gal)
Pre-frac Acid 01*	Acid prior to HF	34,000
Pre-frac Acid 02	Acid prior to HF	73,000
Pre-frac Acid 03	Acid prior to HF	5,000
Foam frac 01*	TW	5,340
	XLF	22,082
	TW + XLF (total)	27,422
Gel frac 01	XLF	1,915,000
Hybrid frac 01*	LF	170,000
	WF	4,500,000
	LF + WF (total)	4,670,000
Hybrid frac 02	TW	816,750
	XLF	2,329,000
	TW + XLF (total)	3,145,750
Hybrid frac 03	LF	29,203
	XLF	97,000
	LF+XLF (total)	126,203
Hybrid frac 04	TW	393,700
	Flush	461,993
	XLF	2,154,500
	TW+XLF+Flush (total)	3,010,193
Hybrid frac 05	TW	849,000
	XLF	1,247,100
	TW+XLF (total)	2,096,100
Hybrid frac 06	TW	7,000
	LF	175,680
	XLF	1,179,324
	LF+XLF+TW (total)	1,362,004
Water frac 01*	WF	4,500,000
Water frac 02	WF	4,500,000
Water frac 03	WF	7,310,000
Water frac 04	Flush	204,600
	LF	502,200
	LF+Flush (total)	706,800

Notes: Treated Water (TW), Linear Fluid (LF), Cross-Linked Fluid (XLF), Water Frac (WF)

*Systems likely to be used for HF activities in the Marcellus Shale formation.

Table 4. Organic Constituents in Typical HESI HF Fluid Systems and Hazard Quotients

Chemical	CAS Number	Estimated Upper Bound Flowback Concentration ¹ (µg/L)	Estimated Upper Bound Concentration in POTW ² (µg/L)		Water Solubility ³ (µg/L)	Solubility Source ⁷	RBC ⁴ (µg/L)	HQ ⁵	
			DAF = 100	DAF = 500				DAF = 100	DAF = 500
Acetic anhydride	108-24-7	6,455,842	64,558	12,912	120,000,000	E	7,026,157	9E-03	2E-03
Carboxymethylhydroxypropyl guar	68130-15-4	5,267,613	52,676	10,535	NA	NA	NA	NA	NA
Acetic acid	64-19-7	4,303,895	43,039	8,608	1,000,000,000	E	25,068,258	2E-03	3E-04
Phosphonic acid, [[[(phosphonomethyl)imino]bis[2,1-ethanediylnitri]bis(methylene)]]tetrakis-, ammonium salt	70714-66-8	3,894,092	38,941	7,788	1,000,000,000	M	52,086,696	7E-04	1E-04
Guar gum	9000-30-0	3,490,851	34,909	6,982	NA	NA	NA	NA	NA
Ginnamaldehyde	104-55-2	3,169,750	31,697	6,339	1,420,000	E	373,515	8E-02	2E-02
Methanol	67-56-1	3,063,037	30,630	6,126	1,000,000,000	E	20,025,000	2E-03	3E-04
Naphtha, hydrotreated heavy	64742-48-9	2,831,831	220	220	220	E	949	2E-01	2E-01
Isopropanol	67-63-0	2,774,519	27,745	5,549	1,000,000,000	E	25,074,936	1E-03	2E-04
Naphtheneic acid ethoxylate	68410-62-8	2,572,951	25,730	5,146	2,846,100	M	793,207	3E-02	6E-03
Alkyl [C14-C16] olefin sulfonate, sodium salt	68439-57-6	2,359,022	23,590	4,718	400,000,000	E	22,836,089	1E-03	2E-04
Chloromethylnaphthalene quinoline quaternary amine	15619-48-4	1,590,803	15,908	3,182	10,088,000	M	1,750,203	9E-03	2E-03
2-Benzylisoquinolinium chloride	35674-56-7	1,193,596	11,936	2,387	10,088,000	M	1,750,203	7E-03	1E-03
Potassium formate	590-29-4	437,030	4,370	874	714,000,000	E	22,206,624	2E-04	4E-05
Polyoxylated fatty amine salt	61791-26-2	1,185,692	1,981	1,981	1,981	M	6,487	3E-01	3E-01
Alcohols, C12-16, ethoxylated	68551-12-2	1,045,385	586	586	586	M	1,849	3E-01	3E-01
Ethylene glycol monobutyl ether	111-76-2	931,193	9,312	1,862	1,000,000,000	E	31,132,506	3E-04	6E-05
Ethylenediaminetetraacetic acid, diammonium copper salt	67989-88-2	884,509	8,845	1,769	1,000,000	E	415,307	2E-02	4E-03
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2	856,536	8,565	1,713	1,000,000,000	E	39,887,563	2E-04	4E-05
Ethanol	64-17-5	729,702	7,297	1,459	1,000,000,000	E	23,984,503	3E-04	6E-05
Amines, coco alkyl, ethoxylated	61791-14-8	616,560	6,166	1,233	1,241,600	M	488,097	1E-02	3E-03
Poly (acrylamide-co-acrylic acid), partial sodium salt	62649-23-4	443,486	4,435	887	NA	NA	NA	NA	NA
Ammonium acetate	631-61-8	660,754	6,608	1,322	14,800,000,000	E	169,667,755	4E-05	8E-06
Diethylene glycol	111-46-6	310,398	3,104	621	1,000,000,000	E	30,078,427	1E-04	2E-05
Formaldehyde polymer with methyl oxirane, 4-nonylphenol and oxirane	63428-92-2	253,595	2,536	507	NA	NA	NA	NA	NA
Hydrotreated light petroleum distillate	64742-47-8	238,433	3.7	3.7	3.7	E	65	6E-02	6E-02
Diethylenetriamine	111-40-0	208,521	2,085	417	1,000,000,000	E	29,808,292	7E-05	1E-05
Triethanolamine zirconate	101033-44-7	176,136	1,761	352	1,000,000,000	M	54,602,160	3E-05	6E-06
Fatty acids, coco, ethoxylated	61791-29-5	168,970	1,690	338	122,120	M	102,012	2E-02	3E-03
Fatty acids, coco, reaction products with ethanolamine, ethoxylated	61791-08-0	168,970	1,690	338	2,240,200	M	812,870	2E-03	4E-04
Terpene hydrocarbon by-products	68956-56-9	136,812	1,368	274	NA	NA	NA	NA	NA
Citrus, extract	94266-47-4	136,812	1,368	274	13,800	E	16,147	8E-02	2E-02
Alcohols, C14-C15, ethoxylated	68951-67-7	133,446	56	56	56	M	459	1E-01	1E-01
Quaternary ammonium compounds, alkylbenzyl(dimethyl), chlorides	8001-54-5	118,653	0.1	0.1	0.14	M	9	2E-02	2E-02
Reaction product of acetophenone, formaldehyde, thiourea and	68527-49-1	112,984	1,130	226	6,130,000	E	979,586	1E-03	2E-04
Castor oil, ethoxylated	61791-12-6	112,693	1,127	225	NA	NA	NA	NA	NA
Sodium formate	141-53-7	107,111	1,071	214	435,000,000	E	14,811,396	7E-05	1E-05
Cobalt acetate	71-48-7	104,400	1,044	209	166,000,000	E	10,448,180	1E-04	2E-05
Amines, coco alkyl, ethoxylated	61790-12-3	988,077	9,881	1,976	12,600	E	19,167	5E-01	1E-01
Heavy aromatic petroleum naphtha	64742-94-5	96,094	961	192	31,000	E	27,455	4E-02	7E-03

Table 4. Organic Constituents in Typical HESI HF Fluid Systems and Hazard Quotients

Chemical	CAS Number	Estimated Upper Bound Flowback Concentration ¹ (ug/L)	Estimated Upper Bound Concentration in POTW ² (ug/L)		Water Solubility ³ (ug/L)	Solubility Source ⁷	RBC ⁴ (ug/L)	HQ ⁵	
			DAF = 100	DAF = 500				DAF = 100	DAF = 500
			Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4				74,557	746
Formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane	29516-47-0	72,456	725	145	NA	NA	NA	NA	NA
Ethoxylated branched C13 alcohol	78330-21-9	71,445	510	143	510	M	2,022	3E-01	7E-02
Quaternary ammonium compounds, bis(hydrogenated tallow Propargyl alcohol	68953-58-2	68,627	686	137	NA	NA	NA	NA	NA
Terpenes and Terpenoids, sweet orange-oil	107-19-7	53,378	534	107	1,000,000,000	E	24,522,740	2E-05	4E-06
Propanol	68647-72-3	41,764	418	84	7,570	E	10,734	4E-02	8E-03
Nonylphenol ethoxylated	71-23-8	38,802	388	78	1,000,000,000	E	7,199,980	5E-05	1E-05
Polyethyleneimine	127087-87-0	36,228	362	72	16,208	M	26,225	1E-02	3E-03
Glycerine	9002-98-6	30,567	306	65	1,000,000,000	E	22,539,068	1E-05	3E-06
Lactose	56-81-5	27,045	270	54	111,000,000	E	28,745,051	1E-05	2E-06
Sodium carboxymethyl cellulose	63-42-3	8,998	90	18	683,000,000	E	9,813,633	3E-05	6E-06
Tributyl tetradecyl phosphonium chloride	81741-28-8	24,367	243.7	48.7	800,000,000	E	27,494,613	2E-04	3E-05
1-Hexadecene	68155-20-4	23,843	238	48	1,058	M	3,874	6E-02	1E-02
Fatty alcohol polyglycol ether surfactant	629-73-2	21,351	0.4	0.4	0.40	M	16	3E-02	3E-02
Alcohols, C10-12, ethoxylated	9043-30-5	19,810	213	43	406,100	M	230,952	9E-04	2E-04
2-Bromo-2-nitro-1,3-propanediol	67254-71-1	18,009	198	40	4,000	E	7,685	3E-02	5E-03
1-Octadecene	52-51-7	13,345	180	36	250,000,000	E	14,352,312	1E-05	3E-06
Formaldehyde	112-88-9	11,765	0.04	0.04	0.038	M	3	1E-02	1E-02
Polyethylene glycol oleate ester	50-00-0	10,805	118	24	400,000,000	E	10,770,069	1E-05	2E-06
Naphthalene	91-20-3	10,778	108	22	31,000	E	27,455	4E-03	8E-04
Sorbitan, mono-9-octadecenoate, (Z)	1338-43-8	4,769	48	10	9,653	M	18,274	3E-03	5E-04
Sorbitan monooleate polyoxyethylene derivative	9005-65-6	3,179	32	6.4	25,013,000	M	5,160,066	6E-06	1E-06
Hemicellulase enzyme	9012-54-8	3,005	30	6.0	NA	NA	NA	NA	NA
1,2,4 Trimethylbenzene	95-63-6	1,811	18	3.6	57,000	E	40,697	4E-04	9E-05
1-Tetradecene	1120-36-1	890	0.4	0.4	0.4	E	15	3E-02	3E-02
1-Eicosene	3452-07-1	890	0.004	0.004	0.0036	M	1	5E-03	5E-03
Sodium glycollate	2836-32-0	155	2	0.3	1,000,000,000	M	29,324,788	5E-08	1E-08
C.I. Pigment Orange 5	3468-63-1	291	2.9	0.6	6.8	E	122	2E-02	5E-03

Notes:

- 1 - Flowback concentrations were conservatively assumed to be the maximum constituent wellhead concentrations across all typical HESI HF fluid systems. See report text for further discussion.
- 2 - Concentration in POTW = Flowback concentration/POTW DAF or the water solubility limit if the diluted concentration exceeds solubility limit.
- 3 - Lowest experimental value. If no experimental value was available, water solubility was modeled using the WATERNT Method from EPA's Epi Suite Software package (v 4.10) [except for CAS # 81741-28-8 was not found in EpiSuite and modeled using CSLogWS™ in ChemSilico]
- 4 - RBC = Risk-Based Concentration. Experimental values for methanol, propanol, ethanol, and tributyl tetradecyl phosphonium chloride (using trihexyl tetradecyl phosphonium bromide as surrogate). Modeled values for other organic compounds based on (IC50) from Trevizo and Nirmalakhandan (1999).
- 5 - HQ = Hazard Quotient = C_{POTW}/RBC
- 6 - Evaluation of potential POTW microorganism risks not required for inorganic and conventional wastewater constituents - see text.
- 7 - E - Experimental; M - Modeled

NA - Not available

3.3 Microorganism Toxicity Benchmarks

In order to characterize the potential for upset conditions, the upper-bound concentrations described in Section 3.2 were compared to toxicity benchmarks for microorganisms. These benchmarks were derived as follows.

As described previously, the POTW treatment process occurs in a series of stages, where removal of organic matter (and perhaps nutrients) occurs in secondary and possibly higher level (*e.g.*, tertiary) treatment stages. Organic materials in a municipal POTW are commonly removed by a process of mineralization,¹² accomplished by an assortment of microorganisms. Municipal wastewater normally contains readily biodegradable organic substances, however, in some cases, wastewater may also contain synthetic organic chemicals. Under some conditions, these synthetic organic constituents could potentially cause upset conditions in a POTW's biological treatment stages.

In order to assess the potential for upset conditions, we developed "risk based concentrations," or RBCs, for the various constituents listed in Table 2 and Table 4. These RBCs provide estimates of a chemical concentration threshold below which adverse effects on microorganisms used in POTW treatment processes would not be expected. The RBCs were derived using the following approach:

- *Estimation from Measured Toxicity Data* – when available, studies that provided microbial toxicity data on flowback constituents were used to derive RBCs.
- *Estimation from Quantitative Structure-Activity Relationships (QSARs)* – when experimental data were not available, we used a method for estimating microbial RBCs that relates chemical solubility to toxicity.

Measured toxicity data from which RBCs were determined were available for the following constituents: benzene, ethyl benzene, toluene, xylene, methanol, propanol, and ethanol. For other constituents, a QSAR was used to predict RBCs. The use of QSARs to estimate chemical toxicity (and by extension RBCs) is an approach that is routinely adopted by the U.S. Environmental Protection Agency (US EPA) when measured data are limited or unavailable. For example, the US EPA Office of Pollution Prevention and Toxics (OPPT) has developed its QSAR model (called ECOSAR-Ecological

¹² Mineralization is the conversion of substances from an organic to inorganic form, *e.g.*, the conversion of organic carbon to CO₂. Mineralization is the method by which POTWs remove organic matter from wastewater.

Structure Activity Relationship) to fill data gaps where little or no experimental measured data exists.¹³

The QSAR used for the purposes of this analysis predicts the inhibitory concentration (IC₅₀)¹⁴ reported to have an effect on activated sludge, methanogens, nitrobacteria, or two commercial bacterial cultures (Polytox and Microtox). Predicted IC₅₀ values were calculated from chemical solubility by using the following equation (Trevizo and Nirmalakhandan, 1999) and these IC₅₀ values were used as the RBCs for constituents that did not have measured toxicity data available.

$$\log (IC_{50}, mM/l) = 0.68 \log (Solubility, mM/l) - 0.25$$

The relationship is a statistically significant linear regression between experimental IC₅₀ data and water solubility for 72 compounds whose solubilities span 8 orders of magnitude (*i.e.*, applicable to a broad range of constituents) (Trevizo and Nirmalakhandan, 1999). RBCs for all organic compounds are shown in Table 2 (measured flowback constituents) and Table 4 (constituents in typical HESI HF systems).

3.4 Risk Characterization

Potential risks to microorganisms used in POTW treatment processes were quantified by calculating a Hazard Quotient (HQ), relating the estimated concentrations of the various flowback constituents in a typical POTW (referred to as “exposure point concentrations” because these are the constituent concentrations to which the microorganisms could be exposed) to the RBCs (discussed in section 3.3, above). This Hazard Quotient (ratio of an exposure point concentration to an RBC) approach is standard practice in ecological risk assessments when evaluating potential chemical impacts to biological organisms. The Hazard Quotient is simply:

$$HQ = \frac{C_{POTW}}{RBC} \quad (3-2)$$

The numerator in this equation (C_{POTW}) was calculated using Equation (3-1). Risks were quantified for two scenarios as described in Section 3.2, using both a median DAF and a high-end DAF to estimate a potential range of flowback constituent concentrations in a POTW. For both scenarios, the conservative,

¹³ <http://www.epa.gov/oppt/newchems/tools/ecosartechfinal.pdf>

¹⁴ The IC₅₀ is a measure of the effectiveness of a chemical in inhibiting biological or biochemical function. For instance, in a Microtox assay, it is the concentration of a chemical at which 50% reduction in bioluminescence by marine bacteria occurs.

maximum constituent concentrations in flowback, discussed in Section 3.2 (see Table 2 and Table 4), were used.

An HQ value of less than or equal to 1 indicates that adverse effects on POTW microorganisms are unlikely, whereas an HQ value greater than 1 indicates that effects cannot be ruled out and additional evaluation may be warranted. The calculated HQs for measured flowback constituents are presented in Table 2 and the calculated HQs for flowback assuming typical HESI HF wellhead concentrations are presented in Table 4. All of the constituent-specific HQs are less than 1 (*i.e.*, $HQ < 1$) – in fact, none of the HQs is greater than 0.3 – indicating that none of the organic constituents potentially present in the flowback would be at concentrations that are expected to upset the POTW treatment process.

In addition to calculating HQs for individual organic flowback constituents, we also summed the HQs for constituents that could potentially be used together in various HF fluid systems to estimate their potential cumulative impact. The sum of the HQs yields a whole-system "Hazard Index" for the typical HESI HF systems (Table 5). While this approach is conventional in risk assessments, we note that it is highly conservative for the following reasons:

- We have used maximum constituent concentrations in flowback, thereby summing "maximum HQs" to yield the Hazard Index. It is highly implausible that all constituents would be found at a POTW at their respective maximum concentration simultaneously.
- We have assumed that HF constituents will be present in flowback at the same concentrations that are found at the wellhead. As discussed in Section 3.2, there are a number of mechanisms that will retain and/or dilute HF constituents, thus resulting in much lower concentrations of HF constituents in flowback.
- Summing HQs to yield a Hazard Index is only meaningful when chemicals exhibit the same toxicological effect, or the toxicological endpoint is sufficiently similar, which is unlikely for the array of chemicals in flowback.

Despite the extremely conservative approach adopted in this assessment, all of the cumulative Hazard Indices for the HESI HF systems are less than 1 (*i.e.*, $HI < 1$) for either of the DAFs (Table 5); in fact none of the cumulative Hazard Indices exceeds 0.6. We note further that any of the "pre-frac acid" formulations identified in Table 3¹⁵ can be used with the various fluid systems or the HF operation can be conducted without the use of a pre-frac acid. Therefore, separate cumulative Hazard Indices were calculated for each fluid system assuming the use of each of the pre-frac acid formulations as well as the

¹⁵ In many cases, an HF job will begin with a "pre-frac acid" stage in which an acid formulation is pumped down the well to clean it out following drilling, casing and cementing before the pumping of the frac fluids starts.

use of a fluid system without any pre-frac acid stage, thus giving the reported range of Hazard Indices for each fluid system in Table 5.

These results (*i.e.*, all HQs<1 and all HIs<1) indicate that flowback constituents, particularly the organic constituents that may be associated with HF fluids, are not expected to upset the POTW biological treatment process. This conclusion is further bolstered by the many highly conservative assumptions made in our calculations.

Table 5. POTW Microorganism Hazard Indices for Typical HESI HF Fluid Systems

HESI HF System	Hazard Index (Sum of HQs)	
	DAF = 100	DAF = 500
Foam frac 01	0.2 - 0.6	0.04 - 0.1
Gel frac 01	0.04 - 0.07	0.01 - 0.01
Hybrid frac 01	0.01 - 0.02	0.002 - 0.004
Hybrid frac 02	0.1 - 0.1	0.02 - 0.03
Hybrid frac 03	0.05 - 0.3	0.01 - 0.06
Hybrid frac 04	0.2 - 0.2	0.04 - 0.04
Hybrid frac 05	0.3 - 0.3	0.06 - 0.07
Hybrid frac 06	0.1 - 0.2	0.03 - 0.04
Water frac 01	0.2 - 0.2	0.03 - 0.03
Water frac 02	0.2 - 0.2	0.03 - 0.03
Water frac 03	0.1 - 0.1	0.02 - 0.02
Water frac 04	0.2 - 0.3	0.05 - 0.06

Range of HI values reflects different Pre-Frac acid formulations used.

4 Conclusion

We evaluated the potential for flowback constituents to upset treatment processes at a typical POTW. Our results, examining a wide range of flowback constituents and a range of dilution factors within a POTW, indicate that organic constituents in flowback are unlikely to impair POTW treatment processes. In our analysis we adopted several notable conservative assumptions that likely overstate potential constituent concentrations in flowback. For example, we assumed that the HF constituents would be recovered in flowback at 100% of the concentration as injected into the subsurface. Yet, in all likelihood, many of the HF constituents will more likely dissipate due to chemical reactions and/or adsorption and dilution in the shale formation. Similarly, our analysis of Marcellus flowback samples reported in the revised dSGEIS is based on the maximum detected concentrations of flowback constituents. Using these conservative assumptions, the results of this analysis indicate that the appropriateness of routine detailed headworks analysis proposed in the revised dSGEIS should be reconsidered with respect to organic constituents in flowback – our analysis indicates little likelihood for these constituents to upset POTW treatment processes.

5 References

Gradient. 2009. Evaluation of Potential Impacts of Hydraulic Fracturing Flowback Fluid Additives on Microbial Processes in Publicly-Owned Treatment Works (POTWs). Prepared for Halliburton Energy Services, Inc. for Submission to New York State Dept. of Environmental Conservation.

New York State Dept. of Environmental Conservation (NYSDEC). 2009. "Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program: Well Permit Issuance for Horizontal Drilling and High-Volume Hydraulic Fracturing to Develop the Marcellus Shale and other Low-Permeability Gas Reservoirs (Draft). Division of Mineral Resources, Bureau of Oil & Gas Regulation.

New York State Dept. of Environmental Conservation (NYSDEC). 2011. "Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program: Well Permit Issuance for Horizontal Drilling and High-Volume Hydraulic Fracturing to Develop the Marcellus Shale and other Low-Permeability Gas Reservoirs (Revised Draft). Division of Mineral Resources, Bureau of Oil & Gas Regulation.

Trevizo, C; Nirmalakhandan, N. 1999. "Prediction of microbial toxicity of industrial organic chemicals." *Water Science and Technology* 39(10-11):63-69.

United States Environmental Protection Agency (US EPA). 2011. Regulating Natural Gas Drilling in the Marcellus Shale under the NPDES Program. Office of Wastewater Management. Memorandum from James A. Hanlon to Water Division Directors. Attachment contains Frequently Asked Questions (FAQs) concerning wastewater issues.

United States Environmental Protection Agency (US EPA). 2011. Methodology Document for the Ecological Structure-Activity Relationship Model (ECOSAR) Class Program. Office of Pollution Prevention and Toxics. Washington DC. June 2011.