

Water Consulting Services in Support of the Supplemental Generic  
Environmental Impact Statement for Natural Gas Production

NYSERDA Contract PO Number 10666

**WATER-RELATED ISSUES ASSOCIATED WITH GAS  
PRODUCTION IN THE MARCELLUS SHALE:**

**Additives Use**  
**Flowback Quality and Quantities**  
**Regulations**  
**On-site Treatment**  
**Green Technologies**  
**Alternate Water Sources**  
**Water Well-Testing**

Prepared by



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# **1 INTRODUCTION AND SCOPE**

## **1.1 Introduction**

The Marcellus Shale formation has been identified as a potentially major source of natural gas. The core formation extends over an eight state area, including parts of New York State. The formation is exposed at the surface in some locations and at depths greater than 7,000 feet at other locations.

In 1992, the New York State Department of Environmental Conservation (NYSDEC) issued a Generic Environmental Impact Statement (GEIS) that provides a comprehensive review of the potential environmental impacts of oil and gas drilling and production and how they may be mitigated. NYSDEC is now preparing a second draft Supplemental GEIS (dSGEIS) to assess issues unique to drilling and high-volume hydraulic fracturing in the Marcellus Shale area. The New York State Energy Research and Development Authority (NYSERDA) is assisting NYSDEC by developing information and data needed for the dSGEIS. NYSERDA has contracted several consultants to research, review, compile, and provide to NYSERDA reports that address different aspects of the final scope for the dSGEIS on the Oil, Gas and Solution Mining Regulatory Program, which was developed by NYSDEC. The SGEIS will be issued by the NYSDEC to establish State Environmental Quality Review (SEQR) thresholds for permitting horizontal drilling and high-volume hydraulic fracturing projects to develop the Marcellus Shale and other low permeability gas reservoirs.

The process of high-volume hydraulic fracturing uses relatively large volumes of water, from about 0.5 to 6 million gallons per well. Water is typically withdrawn from surface water or groundwater sources and stored at each well pad or at centralized facilities until ready to be used. The water is then mixed with proprietary concentrations of proppant and other additives (the mixture is referred to as fracturing fluid), and pumped down into the well at high pressure to fracture the shale. A portion of the fracturing fluid returns to the surface as “flowback” fluid<sup>1</sup>, which requires appropriate treatment and disposal.

This report addresses the following topics related to Marcellus Shale operations:

- a. Fracturing fluid additives
- b. Flowback fluids
- c. Sufficiency of regulations and guidelines
- d. On-site flowback fluids treatment or recycling technologies
- e. Potential ‘green’ (environmentally-friendly) hydraulic fracturing technologies
- f. Alternate water sources for hydraulic fracturing operations, and
- g. Water well sampling needs.

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<sup>1</sup> Independent Oil & Gas Association of New York (IOGA NY) refers to the returning fracturing fluids as produced water. This report distinguishes between flowback and produced water as defined in Section 3-1.

The scope of review for each of these topics is briefly described below.

## **1.2 Report Outline**

Section 2 provides a review of fracturing fluid additives used in drilling/fracturing operations; Section 3 provides a review of flowback fluid volumes and composition. Both of these sections draw on publicly available information and from proprietary data from service companies and operators received via NYSDEC under a confidentiality agreement. In addition, Section 3 includes a summary of the Marcellus Shale Coalition (MSC) study findings. In order to protect industry and trade secrets, these two sections present broad classes of inputs or the generic constituents of additives or flowback, but not the chemical suppliers, product names or the product compositions.

Section 4 provides a review of federal and New York State regulations and guidelines related to water that may impact the oil and gas industry. This section compares the list of parameters presently known to be in additives and analytical results for flowback with parameters regulated by the Safe Drinking Water Act (SDWA), pollutants regulated by the State Pollutant Discharge Elimination System (SPDES) program, or that are addressed in guidance through the Technical & Operational Guidance Series 1.1.1 (TOGS111).

Section 5 surveys on-site treatment or recycling technologies that may potentially be available for operations in the Marcellus Shale.

Section 6 surveys ‘environmentally-friendly’ hydraulic fracturing technologies and chemicals, and draws experiences from gas and oil exploration in the North Sea.

Section 7 surveys potential alternate water sources that may be utilized for hydraulic fracturing operations.

Section 8 surveys existing private water well sampling, testing, and monitoring requirements in other states with Marcellus Shale type development activity. This section identifies potential additional requirements that may be applied within New York State for private water well sampling, testing, and monitoring. This section also identifies potential compounds/elements for testing in typical private water wells in New York State in baseline and post-drilling modes.

Section 9 summarizes the findings and lists limitations of the study.

Section 10 provides a list of references.



## **2 FRACTURING FLUID ADDITIVES**

### **2.1 Introduction**

Hydraulic fracturing is a process whereby a water, proppant and additives mixture (fracturing fluid) is pumped down a well at high pressure. The force of the injection fractures the underground rock (shale formation) allowing natural gas to seep through the fractures into the wellbore and up to the surface.

Hydraulic fracturing fluid consists of water, a “proppant” (a material such as sand that keeps the opened fractures from resealing after the fracturing fluid vacates the space), and a relatively small amount (< 1 percent by volume) of several types of chemical additives. The additives serve a number of purposes listed below. After fracturing the shale, a variable percentage of the fracturing fluid returns to ground surface as flowback.

### **2.2 Desirable Properties of Fracturing Fluids**

Additives are used in hydraulic fracturing operations to elicit certain properties / characteristics that would aide and enhance the operation. The desired properties / characteristics include [1, 2]:

- Non-reactive
- Non-flammable
- Minimal residuals
- Minimal potential for scale or corrosion.
- Low entrained solids
- Neutral pH (pH 6.5 – 7.5) for maximum polymer hydration
- Limited formation damage
- Appropriately modify properties of water to carry proppant deep into the shale
- Economical to modify fluid properties
- Minimal environmental effects

### **2.3 Classes of Additives**

Table 2-1 lists the types, purposes and examples of additives that have been proposed to date for use in hydraulic fracturing of gas wells in New York State.

**Table 2-1 - Types and Purposes of Additives Proposed for Use in New York State**

Additive Type	Description of Purpose	Examples of Chemicals <sup>2</sup>
Proppants	“Props” open fractures and allows gas / fluids to flow more freely to the well bore	Sand [Sintered bauxite; zirconium oxide; ceramic beads]
Acid	Cleans up perforation intervals of cement and drilling mud prior to fracturing fluid injection, and provides accessible path to formation	Hydrochloric acid (HCl, 3% to 28%) or muriatic acid
Breaker	Reduces the viscosity of the fluid in order to release proppant into fractures and enhance the recovery of the fracturing fluid	Peroxydisulfates
Bactericide / Biocide / Antibacterial Agent	Inhibits growth of organisms that could produce gases (particularly hydrogen sulfide) that could contaminate methane gas. Also prevents the growth of bacteria which can reduce the ability of the fluid to carry proppant into the fractures	Gluteraldehyde; 2,2-Dibromo-3-nitropropionamide
Buffer / pH Adjusting Agent	Adjusts and controls the pH of the fluid in order to maximize the effectiveness of other additives such as crosslinkers	Sodium or potassium carbonate; acetic acid
Clay Stabilizer / Control / KCl	Prevents swelling and migration of formation clays which could block pore spaces thereby reducing permeability	Salts (e.g., tetramethyl ammonium chloride, Potassium chloride (KCl))
Corrosion Inhibitor (including Oxygen Scavengers)	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing fluids that contain acid)	Methanol; ammonium bisulfate for Oxygen Scavengers
Crosslinker	Increases fluid viscosity using phosphate esters combined with metals. The metals are referred to as crosslinking agents. The increased fracturing fluid viscosity allows the fluid to carry more proppant into the fractures.	Potassium hydroxide; Borate salts
Friction Reducer	Allows fracturing fluids to be injected at optimum rates and pressures by minimizing friction	Sodium acrylate-acrylamide copolymer; polyacrylamide (PAM); petroleum distillates
Gelling Agent	Increases fracturing fluid viscosity, allowing the fluid to carry more proppant into the fractures	Guar gum; petroleum distillates
Iron Control	Prevents the precipitation of metal oxides which could plug off the formation	Citric acid
Scale Inhibitor	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could plug off the formation	Ammonium chloride; ethylene glycol
Solvents	Additive which is soluble in oil, water & acid-based treatment fluids which is used to control the wettability of contact surfaces or to prevent or break emulsions	Various aromatic hydrocarbons
Surfactant	Reduces fracturing fluid surface tension thereby aiding fluid recovery	Methanol; isopropanol; ethoxylated alcohol

<sup>2</sup> Chemicals in brackets [ ] have not been proposed for use in the State of New York to date, but are known to be used in other states or shale formations.

## 2.4 Composition of Fracturing Fluids

The composition of the fracturing fluid used may vary from one geologic basin/formation to another in order to meet the specific needs of each operation; but the range of additive-types available for potential use remains the same. There are a number of different products for each additive type; however, only one product of each type is typically utilized in any given gas well. The selection may be driven by the formation and potential interactions between additives. Additionally not all additive types will be utilized in every fracturing job.

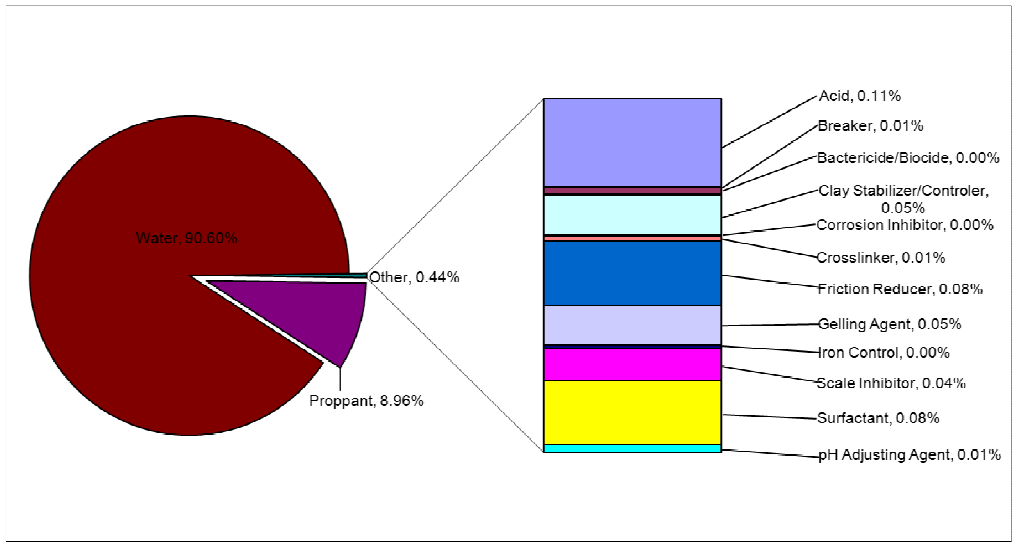
Figure 2-1, Figure 2-2 and Figure 2-3 are three sample compositions, by weight, of fracturing fluids. Figure 2-1 [3] is based on data from the Fayetteville Shale<sup>3</sup>; Figure 2-2 and Figure 2-3 [4] are based on data from Marcellus Shale development in Pennsylvania. Based on this data, between approximately 80 and 90 percent of the fracturing fluid is water; between approximately 8 and 15 percent is proppant; the remainder, typically less than 1 percent, consists of chemical additives listed above. The specific fracturing fluid composition, types of additives and specific products used would depend on the location and the operator.

Barnett Shale is considered to be the first instance of extensive hydraulic fracturing technology use in horizontal shale wells; the technology was later applied in other areas such as the Fayetteville Shale and the Haynesville Shale. Data collected from applications to drill Marcellus Shale wells in New York indicate that the typical fracturing fluid composition for operations in the Marcellus Shale is similar to that provided for the Fayetteville Shale. Even though no horizontal wells have been drilled in the Marcellus Shale in New York, applications filed to date indicate that it is realistic to expect that the composition of fracturing fluids used for developing the Marcellus Shale in New York would be similar to the compositions used in the Fayetteville Shale and Marcellus Shale in Pennsylvania.

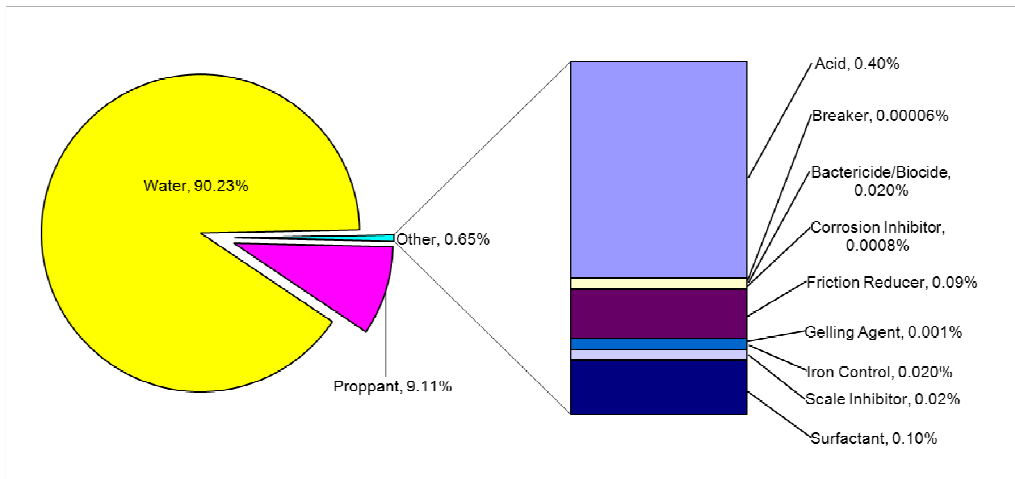
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<sup>3</sup> Similar to the Marcellus Shale, the Fayetteville Shale is a marine shale rich in unoxidized carbon (i.e. a black shale). The two shales are at similar depths, and vertical and horizontal wells have been drilled/fractured in both shales.

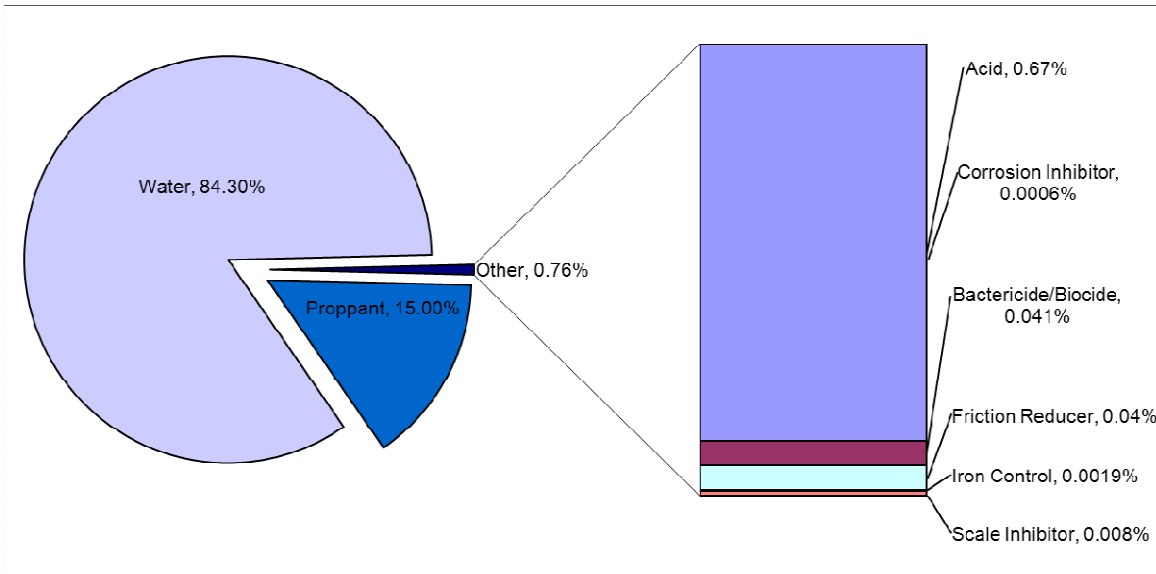
**Figure 2-1 - Sample Fracturing fluid Composition (12 additives), by Weight, from Fayetteville Shale**



**Figure 2-2 - Sample Fracturing fluid Composition (9 additives), by Weight, from Marcellus Shale**



**Figure 2-3 - Sample Fracturing fluid Composition (6 additives), by Weight, from Marcellus Shale**



Each product within these thirteen classes of additives may be made up of one or more chemical constituents. Table 2-2 is a list of chemical constituents and their CAS numbers, that have been extracted from complete product chemical composition and Material Safety Data Sheets submitted to the NYSDEC. This list is based on over 230 products used or proposed for use in hydraulic fracturing operations in the Marcellus Shale area of New York. It is important to note that several manufacturers / suppliers provide similar products (i.e. chemicals that would serve the same purpose) for any class of additive. Therefore only a handful of chemicals from Table 2-2 would be utilized in a single well. Table 2-2 represents constituents of all hydraulic-fracturing-related additives submitted to NYSDEC to date for potential use in shale wells in the State.

Data provided to NYSDEC to date indicates similar fracturing fluid compositions for vertically and horizontally drilled wells.

**Table 2-2 – Chemical Constituents in Additives<sup>4,5,6</sup>**

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
106-24-1	(2E)-3,7-dimethylocta-2,6-dien-1-ol
67701-10-4	(C8-C18) and (C18) Unsaturated Alkylcarboxylic Acid Sodium Salt
2634-33-5	1,2-Benzisothiazolin-2-one / 1,2-benzisothiazolin-3-one
95-63-6	1,2,4-trimethylbenzene
93858-78-7	1,2,4-Butanetricarboxylic acid, 2-phosphono-, potassium salt
123-91-1	1,4-Dioxane
3452-07-1	1-eicosene
629-73-2	1-hexadecene
104-46-1	1-Methoxy-4-propenylbenzene
124-28-7	1-Octadecanamine, N, N-dimethyl- / N,N-Dimethyloctadecylamine
	1-Octadecanaminium, N,N,N-Trimethyl-, Chloride
112-03-8	/Trimethyloctadecylammonium chloride
112-88-9	1-octadecene
40623-73-2	1-Propanesulfonic acid
1120-36-1	1-tetradecene
95077-68-2	2-Propenoic acid, homopolymer sodium salt
98-55-5	2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol
10222-01-2	2,2-Dibromo-3-nitrilopropionamide
27776-21-2	2,2'-azobis-{2-(imidazolin-2-yl)propane}-dihydrochloride
73003-80-2	2,2-Dobromomalonamide
15214-89-8	2-Acrylamido-2-methylpropanesulphonic acid sodium salt polymer
46830-22-2	2-acryloyloxyethyl(benzyl)dimethylammonium chloride
52-51-7	2-Bromo-2-nitro-1,3-propanediol
111-76-2	2-Butoxy ethanol / Ethylene glycol monobutyl ether / Butyl Cellusolve
1113-55-9	2-Dibromo-3-Nitrilopropionamide /2-Monobromo-3-nitrilopropionamide
104-76-7	2-Ethyl Hexanol
67-63-0	2-Propanol / Isopropyl Alcohol / Isopropanol / Propan-2-ol
26062-79-3	2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-chloride, homopolymer
9003-03-6	2-propenoic acid, homopolymer, ammonium salt
25987-30-8	2-Propenoic acid, polymer with 2 p-propenamide, sodium salt / Copolymer of acrylamide and sodium acrylate
71050-62-9	2-Propenoic acid, polymer with sodium phosphinate (1:1)
66019-18-9	2-propenoic acid, telomer with sodium hydrogen sulfite

<sup>4</sup> Table 2-2 is a list of chemical constituents and their CAS numbers that have been extracted from complete chemical compositions and Material Safety Data Sheets submitted to the NYSDEC.

<sup>5</sup> These are the chemical constituents of all chemical additives proposed to be used in New York for hydraulic fracturing operations at shale wells. Only a few additives will be used in a single well; the list of chemical constituents used in an individual well will be correspondingly smaller.

<sup>6</sup> This list would not include chemicals/products that are exclusively used for drilling.

<sup>7</sup> Chemical Abstracts Service (CAS) is a division of the American Chemical Society. CAS assigns unique numerical identifiers to every chemical described in the literature. The intention is to make database searches more convenient, as chemicals often have many names. Almost all chemical molecule databases today allow searching by CAS number.

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
107-19-7	2-Propyn-1-ol / Propargyl Alcohol
51229-78-8	3,5,7-Triaza-1-azoniatricyclo[3.3.1.1 <sup>3,7</sup> ]decane, 1-(3-chloro-2-propenyl)-chloride,
106-22-9	3,7 - dimethyl-6-octen-1-ol
5392-40-5	3,7-dimethyl-2,6-octadienal
115-19-5	3-methyl-1-butyn-3-ol
104-55-2	3-phenyl-2-propenal
127-41-3	4-(2,6,6-trimethyl-1-cyclohex-2-enyl)-3-buten-2-one
121-33-5	4-hydroxy-3-methoxybenzaldehyde
127087-87-0	4-Nonylphenol Polyethylene Glycol Ether Branched / Nonylphenol ethoxylated / Oxyalkylated Phenol
64-19-7	Acetic acid
68442-62-6	Acetic acid, hydroxy-, reaction products with triethanolamine
108-24-7	Acetic Anhydride
67-64-1	Acetone
79-06-1	Acrylamide
38193-60-1	Acrylamide - sodium 2-acrylamido-2-methylpropane sulfonate copolymer
25085-02-3	Acrylamide - Sodium Acrylate Copolymer /Anionic Polyacrylamide / 2-Propanoic acid
69418-26-4	Acrylamide polymer with N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride / Ethanaminium, N, N, N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride, polymer with 2-propenamide (9Cl)
15085-02-3	Acrylamide-sodium acrylate copolymer
68891-29-2	Alcohols C8-10, ethoxylated, monoether with sulfuric acid, ammonium salt
68526-86-3	Alcohols, C11-14-iso, C13-rich
68551-12-2	Alcohols, C12-C16, Ethoxylated /Ethoxylated alcohol
64742-47-8	Aliphatic Hydrocarbon / Hydrotreated light distillate / Petroleum Distillates / Isoparaffinic Solvent / Paraffin Solvent / Napthenic Solvent
64743-02-8	Alkenes
68439-57-6	Alkyl (C14-C16) olefin sulfonate, sodium salt
9016-45-9	Alkylphenol ethoxylate surfactants
1327-41-9	Aluminum chloride
68155-07-7	Amides, C8-18 and C19-Unsatd., N,N-Bis(hydroxyethyl)
73138-27-9	Amines, C12-14-tert-alkyl, ethoxylated
71011-04-6	Amines, Ditallow alkyl, ethoxylated
68551-33-7	Amines, tallow alkyl, ethoxylated, acetates
1336-21-6	Ammonia
631-61-8	Ammonium acetate
68037-05-8	Ammonium Alcohol Ether Sulfate
7783-20-2	Ammonium bisulfate
10192-30-0	Ammonium Bisulphite
12125-02-9	Ammonium Chloride
7632-50-0	Ammonium citrate
37475-88-0	Ammonium Cumene Sulfonate
1341-49-7	Ammonium hydrogen-difluoride
6484-52-2	Ammonium nitrate

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
7727-54-0	Ammonium Persulfate / Diammonium peroxodisulphate
1762-95-4	Ammonium Thiocyanate
7664-41-7	Aqueous ammonia
12174-11-7	Attapulgite Clay
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex / organophilic clay
71-43-2	Benzene
119345-04-9	Benzene, 1,1'-oxybis, tetrapropylene derivatives, sulfonated, sodium salts
74153-51-8	Benzenemethanaminium, N,N-dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-, chloride, polymer with 2-propenamide
122-91-8	Benzenemethanol,4-methoxy-, 1-formate
1300-72-7	Benzenesulfonic acid, Dimethyl-, Sodium salt /Sodium xylene sulfonate
140-11-4	Benzyl acetate
76-22-2	Bicyclo (2.2.1) heptan-2-one, 1,7,7-trimethyl-
68153-72-0	Blown lard oil amine
68876-82-4	Blown rapeseed amine
1319-33-1	Borate Salt
10043-35-3	Boric acid
1303-86-2	Boric oxide / Boric Anhydride
71-36-3	Butan-1-ol
68002-97-1	C10 - C16 Ethoxylated Alcohol
68131-39-5	C12-15 Alcohol, Ethoxylated
1317-65-3	Calcium Carbonate
10043-52-4	Calcium chloride
1305-62-0	Calcium Hydroxide
1305-79-9	Calcium Peroxide
124-38-9	Carbon Dioxide
68130-15-4	Carboxymethylhydroxypropyl guar
9012-54-8	Cellulase / Hemicellulase Enzyme
9004-34-6	Cellulose
10049-04-4	Chlorine Dioxide
78-73-9	Choline Bicarbonate
67-48-1	Choline Chloride
91-64-5	Chromen-2-one
77-92-9	Citric Acid
94266-47-4	Citrus Terpenes
61789-40-0	Cocamidopropyl Betaine
68155-09-9	Cocamidopropylamine Oxide
68424-94-2	Coco-betaine
7758-98-7	Copper (II) Sulfate
14808-60-7	Crystalline Silica (Quartz)
7447-39-4	Cupric chloride dihydrate
1490-04-6	Cyclohexanol,5-methyl-2-(1-methylethyl)
8007-02-1	Cymbopogon citratus leaf oil
8000-29-1	Cymbopogon winterianus jowitt oil



<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
1120-24-7	Decyldimethyl Amine
2605-79-0	Decyl-dimethyl Amine Oxide
3252-43-5	Dibromoacetonitrile
25340-17-4	Diethylbenzene
111-46-6	Diethylene Glycol
22042-96-2	Diethylenetriamine penta (methylenephonic acid) sodium salt
28757-00-8	Diisopropyl naphthalenesulfonic acid
68607-28-3	Dimethylcocoamine, bis(chloroethyl) ether, diquaternary ammonium salt
7398-69-8	Dimethyldiallylammonium chloride
25265-71-8	Dipropylene glycol
34590-94-8	Dipropylene Glycol Methyl Ether
139-33-3	Disodium Ethylene Diamine Tetra Acetate
64741-77-1	Distillates, petroleum, light hydrocracked
5989-27-5	D-Limonene
123-01-3	Dodecylbenzene
27176-87-0	Dodecylbenzene sulfonic acid
42504-46-1	Dodecylbenzenesulfonate isopropanolamine
50-70-4	D-Sorbitol / Sorbitol
37288-54-3	Endo-1,4-beta-mannanase, or Hemicellulase
149879-98-1	Erucic Amidopropyl Dimethyl Betaine
89-65-6	Erythorbic acid, anhydrous
54076-97-0	Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride, homopolymer
107-21-1	Ethane-1,2-diol / Ethylene Glycol
111-42-2	Ethanol, 2,2-iminobis-
26027-38-3	Ethoxylated 4-nonylphenol
9002-93-1	Ethoxylated 4-tert-octylphenol
68439-50-9	Ethoxylated alcohol
126950-60-5	Ethoxylated alcohol
67254-71-1	Ethoxylated alcohol (C10-12)
68951-67-7	Ethoxylated alcohol (C14-15)
68439-46-3	Ethoxylated alcohol (C9-11)
66455-15-0	Ethoxylated Alcohols
84133-50-6	Ethoxylated Alcohols (C12-14 Secondary)
68439-51-0	Ethoxylated Alcohols (C12-14)
78330-21-9	Ethoxylated branch alcohol
34398-01-1	Ethoxylated C11 alcohol
78330-21-8	Ethoxylated C11-14-iso, C13-rich alcohols
61791-12-6	Ethoxylated Castor Oil
61791-29-5	Ethoxylated fatty acid, coco
61791-08-0	Ethoxylated fatty acid, coco, reaction product with ethanolamine
68439-45-2	Ethoxylated hexanol
9036-19-5	Ethoxylated octylphenol
9005-67-8	Ethoxylated Sorbitan Monostearate
9005-70-3	Ethoxylated Sorbitan Trioleate

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
118-61-6	Ethyl 2-hydroxybenzoate
64-17-5	Ethyl alcohol / ethanol
100-41-4	Ethyl Benzene
93-89-0	Ethyl benzoate
97-64-3	Ethyl Lactate
9003-11-6	Ethylene Glycol-Propylene Glycol Copolymer (Oxirane, methyl-, polymer with oxirane)
75-21-8	Ethylene oxide
5877-42-9	Ethyloctynol
8000-48-4	Eucalyptus globulus leaf oil
61790-12-3	Fatty Acids
68604-35-3	Fatty acids, C 8-18 and C18-unsaturated compounds with diethanolamine
68188-40-9	Fatty acids, tall oil reaction products w/ acetophenone, formaldehyde & thiourea
9043-30-5	Fatty alcohol polyglycol ether surfactant
7705-08-0	Ferric chloride
7782-63-0	Ferrous sulfate, heptahydrate
50-00-0	Formaldehyde
29316-47-0	Formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane
153795-76-7	Formaldehyde, polymers with branched 4-nonylphenol, ethylene oxide and propylene oxide
75-12-7	Formamide
64-18-6	Formic acid
110-17-8	Fumaric acid
65997-17-3	Glassy calcium magnesium phosphate
111-30-8	Glutaraldehyde
56-81-5	Glycerol / glycerine
9000-30-0	Guar Gum
64742-94-5	Heavy aromatic petroleum naphtha
9025-56-3	Hemicellulase
7647-01-0	Hydrochloric Acid / Hydrogen Chloride / muriatic acid
7722-84-1	Hydrogen Peroxide
64742-52-5	Hydrotreated heavy naphthenic (petroleum) distillate
79-14-1	Hydroxy acetic acid
35249-89-9	Hydroxyacetic acid ammonium salt
9004-62-0	Hydroxyethyl cellulose
5470-11-1	Hydroxylamine hydrochloride
39421-75-5	Hydroxypropyl guar
35674-56-7	Isomeric Aromatic Ammonium Salt
64742-88-7	Isoparaffinic Petroleum Hydrocarbons, Synthetic
64-63-0	Isopropanol
98-82-8	Isopropylbenzene (cumene)
68909-80-8	Isoquinoline, reaction products with benzyl chloride and quinoline
8008-20-6	Kerosene
64742-81-0	Kerosine, hydrodesulfurized

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
63-42-3	Lactose
8022-15-9	Lavandula hybrida abrial herb oil
64742-95-6	Light aromatic solvent naphtha
1120-21-4	Light Paraffin Oil
546-93-0	Magnesium Carbonate
1309-48-4	Magnesium Oxide
1335-26-8	Magnesium Peroxide
14807-96-6	Magnesium Silicate Hydrate (Talc)
1184-78-7	methanamine, N,N-dimethyl-, N-oxide
67-56-1	Methanol
119-36-8	Methyl 2-hydroxybenzoate
68891-11-2	Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched
8052-41-3	Mineral spirits / Stoddard Solvent
64742-46-7	Mixture of severely hydrotreated and hydrocracked base oil
141-43-5	Monoethanolamine
44992-01-0	N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride
64742-48-9	Naphtha (petroleum), hydrotreated heavy
91-20-3	Naphthalene
38640-62-9	Naphthalene bis(1-methylethyl)
93-18-5	Naphthalene, 2-ethoxy-
68909-18-2	N-benzyl-alkyl-pyridinium chloride
68139-30-0	N-Cocoamidopropyl-N,N-dimethyl-N-2-hydroxypropylsulfobetaine
7727-37-9	Nitrogen, Liquid form
68412-54-4	Nonylphenol Polyethoxylate
8000-27-9	Oils, cedarwood
121888-66-2	Organophilic Clays
628-63-7	Pentyl acetate
540-18-1	Pentyl butanoate
8009-03-8	Petrolatum
64742-65-0	Petroleum Base Oil
64741-68-0	Petroleum naphtha
101-84-8	Phenoxybenzene
70714-66-8	Phosphonic acid, [[[phosphonomethyl]imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt
8000-41-7	Pine Oil
8002-09-3	Pine Oils
60828-78-6	Poly(oxy-1,2-ethanediyl), a-[3,5-dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-
25322-68-3	Poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy / Polyethylene Glycol
31726-34-8	Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy
24938-91-8	Poly(oxy-1,2-ethanediyl), $\alpha$ -tridecyl- $\omega$ -hydroxy-
9004-32-4	Polyanionic Cellulose
51838-31-4	Polyepichlorohydrin, trimethylamine quaternized
56449-46-8	Polyethylene glycol oleate ester
9046-01-9	Polyethoxylated tridecyl ether phosphate

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
63428-86-4	Polyethylene glycol hexyl ether sulfate, ammonium salt
62649-23-4	Polymer with 2-propenoic acid and sodium 2-propenoate
9005-65-6	Polyoxyethylene Sorbitan Monooleate
61791-26-2	Polyoxylated fatty amine salt
65997-18-4	Polyphosphate
127-08-2	Potassium acetate
12712-38-8	Potassium borate
1332-77-0	Potassium borate
20786-60-1	Potassium Borate
584-08-7	Potassium carbonate
7447-40-7	Potassium chloride
590-29-4	Potassium formate
1310-58-3	Potassium Hydroxide
13709-94-9	Potassium metaborate
24634-61-5	Potassium Sorbate
112926-00-8	Precipitated silica / silica gel
57-55-6	Propane-1,2-diol, or Propylene glycol
107-98-2	Propylene glycol monomethyl ether
68953-58-2	Quaternary Ammonium Compounds
62763-89-7	Quinoline,2-methyl-, hydrochloride
15619-48-4	Quinolinium, 1-(phenylmethyl),chloride
8000-25-7	Rosmarinus officinalis l. leaf oil
7631-86-9	Silica, Dissolved
5324-84-5	Sodium 1-octanesulfonate
127-09-3	Sodium acetate
95371-16-7	Sodium Alpha-olefin Sulfonate
532-32-1	Sodium Benzoate
144-55-8	Sodium bicarbonate
7631-90-5	Sodium bisulfate
7647-15-6	Sodium Bromide
497-19-8	Sodium carbonate
7647-14-5	Sodium Chloride
7758-19-2	Sodium chlorite
3926-62-3	Sodium Chloroacetate
68-04-2	Sodium citrate
6381-77-7	Sodium erythorbate / isoascorbic acid, sodium salt
2836-32-0	Sodium Glycolate
1310-73-2	Sodium Hydroxide
1301-73-2	Sodium hydroxide
7681-52-9	Sodium hypochlorite
7775-19-1	Sodium Metaborate .8H <sub>2</sub> O
10486-00-7	Sodium perborate tetrahydrate
7775-27-1	Sodium persulphate
68608-26-4	Sodium petroleum sulfonate
9003-04-7	Sodium polyacrylate

<b>CAS Number<sup>7</sup></b>	<b>Chemical Constituent</b>
7757-82-6	Sodium sulfate
1303-96-4	Sodium tetraborate decahydrate
7772-98-7	Sodium Thiosulfate
1338-43-8	Sorbitan Monooleate
57-50-1	Sucrose
5329-14-6	Sulfamic acid
68442-77-3	Surfactant: Modified Amine
112945-52-5	Synthetic Amorphous / Pyrogenic Silica / Amorphous Silica
68155-20-4	Tall Oil Fatty Acid Diethanolamine
8052-48-0	Tallow fatty acids sodium salt
72780-70-7	Tar bases, quinoline derivs., benzyl chloride-quaternized
68647-72-3	Terpene and terpenoids
68956-56-9	Terpene hydrocarbon byproducts
533-74-4	Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione /Dazomet
55566-30-8	Tetrakis(hydroxymethyl)phosphonium sulfate (THPS)
75-57-0	Tetramethyl ammonium chloride
64-02-8	Tetrasodium Ethylenediaminetetraacetate
68-11-1	Thioglycolic acid
62-56-6	Thiourea
68527-49-1	Thiourea, polymer with formaldehyde and 1-phenylethanone
68917-35-1	Thuja plicata donn ex. D. don leaf oil
108-88-3	Toluene
81741-28-8	Tributyl tetradecyl phosphonium chloride
68299-02-5	Triethanolamine hydroxyacetate
112-27-6	Triethylene Glycol
52624-57-4	Trimethylolpropane, Ethoxylated, Propoxylated
150-38-9	Trisodium Ethylenediaminetetraacetate
5064-31-3	Trisodium Nitritotriacetate
7601-54-9	Trisodium ortho phosphate
57-13-6	Urea
25038-72-6	Vinylidene Chloride/Methylacrylate Copolymer
7732-18-5	Water
8042-47-5	White Mineral Oil
11138-66-2	Xanthan gum
1330-20-7	Xylene
13601-19-9	Yellow Sodium of Prussiate

**Chemical Constituent**

Aliphatic acids  
Aliphatic alcohol glycol ether  
Alkyl Aryl Polyethoxy Ethanol  
Alkylaryl Sulfonate  
Anionic copolymer  
Aromatic hydrocarbons  
Aromatic ketones

### **Chemical Constituent**

Oxyalkylated alkylphenol  
Petroleum distillate blend  
Polyethoxylated alkanol  
Polymeric Hydrocarbons  
Salt of amine-carbonyl condensate  
Salt of fatty acid/polyamine reaction product  
Sugar  
Surfactant blend  
Triethanolamine

## **2.5 Selection of Additives**

Information available from well operators, service companies, and chemical suppliers indicate that there are a number of breakers, biocides, clay stabilizers, etc. that may be selected for any hydraulic fracturing operation. The different product options may not be interchangeable because of undesirable chemical reactions that may occur between different classes of chemicals. The actual selection of additives is somewhat driven by the specific operation.

Operators have been required to divulge the types of additives, product names, specific chemical constituents, and chemical formulas to be used in a hydraulic fracturing operation before NYSDEC will issue a well permit. The fact that such information is often considered proprietary does not prevent the NYSDEC from requiring full-disclosure of this information. The handling of any information submitted to the NYSDEC and claimed to be a trade secret is governed by the New York State Public Officer's Law and the Department's Records Access Regulations.

## **2.6 Additives Sequence**

Several types of additives may be used in a single well; however, they are not used at the same time. The additives are sequenced to elicit a specific fracturing fluid characteristic at different phases of the operation. A typical sequence may include the following:

- Phase 1: Corrosion inhibitors, iron controls and acids are used in the initial stage to reduce rust formation on steel tubing, well casings, tools, and tanks [5]; to prevent precipitation of metal oxides which could plug the shale; and to improve fluid access into the formation, respectively.
- Phase 2: Gelling agent, crosslinker, and other additives are used in the second stage to improve the fracturing fluid's capacity (typically by increasing viscosity) to carry proppant into the fractures. In addition, bactericide/biocide would be used to prevent the growth of bacteria, which can reduce the ability of the fluid to carry proppant into the fractures [6].

- Phase 3: Once the proppant is conveyed to the formation, the proppant needs to be released into the formation. Therefore a breaker is used to reduce the viscosity of the fluid and release the proppant within the fractures and to enhance the recovery of the fracturing fluid. Use of friction reducers allows fracturing fluids to be injected at optimum rates. Biocides are also used in this stage to inhibit the growth of organisms that could potentially produce gases such as hydrogen sulfide that could contaminate natural gas. A clay stabilizer may be used to prevent swelling and migration of formation clays which could block pore spaces.

Not all types of additives are used in a single well. The combination of additives and specific chemicals used would depend on the particular shale, well and well operator / service company.

## **2.7 Summary**

Large volumes of water and proppant are used in hydraulic fracturing operations. Small quantities of several additives are used to facilitate and enhance fracturing. This section identified 13 classes of additives that may be used in shale fracturing. These 13 classes may encompass over one thousand chemicals used around the globe. Table 2-2 lists the primary constituents found in approximately 230 products used or proposed for use in hydraulic fracturing operations in New York.

## **3 FLOWBACK FLUIDS**

### **3.1 Introduction**

Flowback is one of several waste fluids generated from a gas well. Waste fluids from a gas well may be grouped into several categories: top-hole fluids; bottom hole fluids; stimulation fluids; and production fluids [7].

- Top-hole fluids consist of ‘waste’ fluids generated due to fresh water aquifers that may be encountered within the first few hundred feet of drilling. Top-hole fluids do not intermingle within the well bore the way bottom hole and stimulation fluids do.
- Bottom-hole fluids typically consist of fluids generated due to deep salt water zones encountered.
- Stimulation / fracturing fluids are waste fluids generated due to the water, proppants and other additives pumped into the shale to improve gas recovery.
- Production fluids (or Produced Water) are the waste fluids produced with natural gas after the well is put into production; their composition is typically similar to bottom hole fluids.

The flowback fluids discussed in this section consist mostly of stimulation fluids and bottom-hole fluids.

### **3.2 Flowback Fluid Volume**

The volume of flowback fluid from a gas well depends on a variety of factors, including the particular shale, the depth and age of the well, and the drilling technique (horizontal vs. vertical).

Typical water usage for hydraulic fracturing is approximately 1.5 million gallons (MG) per vertical well and between 2.5 and 5 MG per horizontal well. Limited data indicate that water usage may be as little as 0.5 MG or as much as 3 million gallons (MG) per vertical well and as much as 6 MG per horizontal well.

Based on limited data reported to NYSDEC and information from operators in Pennsylvania, flowback from Marcellus Shale operations, which includes both vertical and horizontal wells, is approximately 20 – 35 percent of fracturing fluids used<sup>8</sup>, with up to 85 percent from a vertical well, and between 10 and 50 percent from horizontal wells reported [9].

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<sup>8</sup> Typical flowback from operations based in Marcellus Shale, as estimated by URS Corporation. These values are consistent with those reported in the MSC Study [9].



### 3.3 Trends in Flowback Fluid Volume

Flowback occurs over 2-3 weeks after fracturing, and the flowback rate changes with time; the actual rate may depend on a variety of factors. Limited time-series data indicates that approximately 60 percent of the total flowback occurs in the first four days after fracturing. After day 4, the daily flowback rate declines sharply to between approximately 2 – 5 percent of the total flowback for approximately 2 weeks.

### 3.4 Flowback Fluid Composition

Flowback fluids include the fracturing fluids pumped into the well, and consist of water and additives discussed in the previous section, any new compounds that may have formed due to reactions between additives, and substances mobilized from within the shale formation due to the fracturing operation. Some portion of the proppant may return to the surface with flowback, but operators strive to minimize proppant return: the ultimate goal of hydraulic fracturing is to convey and deposit the proppant within fractures in the shale to maximize gas flow.

Marcellus Shale is of marine origin and, therefore, contains high levels of salt [5]. This is further evidenced by analytical results of flowback provided to NYSDEC by well operators from operations based in Pennsylvania. The results were in different levels of detail. Some companies provided analytical results for one day for several wells, while other companies provided several analytical results for multiple days of the same well (i.e. time-series). Flowback parameters were organized by Chemicals Abstract Service (CAS) number, whenever available.

Typical classes of parameters present in flowback fluid are [1 and 8]:

- Dissolved Solids (chlorides, sulfates, and calcium)
- Metals (calcium, magnesium, barium, strontium)
- Suspended solids
- Mineral scales (calcium carbonate and barium sulfate)
- Bacteria - acid producing bacteria and sulfate reducing bacteria
- Friction Reducers
- Iron solids (iron oxide and iron sulfide)
- Dispersed clay fines, colloids, and silts
- Acid Gases (carbon dioxide, hydrogen sulfide)

A list of parameters detected in a limited set of analytical results is provided in Table 3-1. Typical concentrations of parameters, based on limited data from PA and WV, are provided in Table 4-6.

**Table 3-1 - Parameters present in a limited set of flowback analytical results<sup>9</sup>**

<b>CAS Number</b>	<b>Parameters Detected in Flowback from PA and WV Operations</b>
00087-61-6	1,2,3-Trichlorobenzene
00095-63-6	1,2,4-Trimethylbenzene
00108-67-8	1,3,5-Trimethylbenzene
00105-67-9	2,4-Dimethylphenol
00087-65-0	2,6-Dichlorophenol
00078-93-3	2-Butanone / Methyl ethyl ketone
00091-57-6	2-Methylnaphthalene
00095-48-7	2-Methylphenol
109-06-8	2-Picoline (2-methyl pyridine)
00067-63-0	2-Propanol / Isopropyl Alcohol / Isopropanol / Propan-2-ol
00108-39-4	3-Methylphenol
00106-44-5	4-Methylphenol
00072-55-9	4,4 DDE
00057-97-6	7,12-Dimethylbenz(a)anthracene
00064-19-7	Acetic acid
00067-64-1	Acetone
00098-86-2	Acetophenone
00107-13-1	Acrylonitrile
00309-00-2	Aldrin
07439-90-5	Aluminum
07440-36-0	Antimony
07664-41-7	Aqueous ammonia
12672-29-6	Aroclor 1248
07440-38-2	Arsenic
07440-39-3	Barium
00071-43-2	Benzene
00050-32-8	Benzo(a)pyrene
00205-99-2	Benzo(b)fluoranthene
191-24-2	Benzo(ghi)perylene
00207-08-9	Benzo(k)fluoranthene
00100-51-6	Benzyl alcohol
07440-41-7	Beryllium
00111-44-4	Bis(2-Chloroethyl) ether
00117-81-7	Bis(2-ethylhexyl)phthalate / Di (2-ethylhexyl) phthalate
07440-42-8	Boron
24959-67-9	Bromide
00075-25-2	Bromoform
07440-43-9	Cadmium
07440-70-2	Calcium
00124-38-9	Carbon Dioxide
00075-15-0	Carbendisulfide
00124-48-1	Chlorodibromomethane
00067-66-3	Chloroform

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<sup>9</sup> This parameter list is a compilation of flowback analytical results provided to NYSDEC by service companies with operations in PA and/or WV.

<b>CAS Number</b>	<b>Parameters Detected in Flowback from PA and WV Operations</b>
07440-47-3	Chromium
07440-48-4	Cobalt
07440-50-8	Copper
00057-12-5	Cyanide
00319-85-7	Cyclohexane (beta BHC)
00058-89-9	Cyclohexane (gamma BHC)
00055-70-3	Dibenz(a,h)anthracene
00075-27-4	Dichlorobromomethane
00084-74-2	Di-n-butyl phthalate
00122-39-4	Diphenylamine
00959-98-8	Endosulfan I
33213-65-9	Endosulfan II
07421-93-4	Endrin aldehyde
00107-21-1	Ethane-1,2-diol / Ethylene Glycol
00100-41-4	Ethyl Benzene
00206-44-0	Fluoranthene
00086-73-7	Fluorene
16984-48-8	Fluoride
00076-44-8	Heptachlor
01024-57-3	Heptachlor epoxide
00193-39-5	Indeno(1,2,3-cd)pyrene
07439-89-6	Iron
00098-82-8	Isopropylbenzene (cumene)
07439-92-1	Lead
07439-93-2	Lithium
07439-95-4	Magnesium
07439-96-5	Manganese
07439-97-6	Mercury
00067-56-1	Methanol
00074-83-9	Methyl Bromide
00074-87-3	Methyl Chloride
07439-98-7	Molybdenum
00091-20-3	Naphthalene
07440-02-0	Nickel
00086-30-6	N-Nitrosodiphenylamine
00085-01-8	Phenanthrene
00108-95-2	Phenol
57723-14-0	Phosphorus
07440-09-7	Potassium
00057-55-6	Propylene glycol
00110-86-1	Pyridine
00094-59-7	Safrole
07782-49-2	Selenium
07440-22-4	Silver
07440-23-5	Sodium
07440-24-6	Strontium
14808-79-8	Sulfate
14265-45-3	Sulfite
00127-18-4	Tetrachloroethylene

<b>CAS Number</b>	<b>Parameters Detected in Flowback from PA and WV Operations</b>
07440-28-0	Thallium
07440-32-6	Titanium
00108-88-3	Toluene
07440-62-2	Vanadium
07440-66-6	Zinc
	2-Picoline
	Alkalinity
	Alkalinity, Carbonate, as CaCO <sub>3</sub>
	Alpha radiation
	Aluminum, Dissolved
	Barium Strontium P.S.
	Barium, Dissolved
	Beta radiation
	Bicarbonates
	Biochemical Oxygen Demand
	Cadmium, Dissolved
	Calcium, Dissolved
	Cesium 137
	Chemical Oxygen Demand
	Chloride
	Chromium (VI)
	Chromium (VI), dissolved
	Chromium, (III)
	Chromium, Dissolved
	Cobalt, dissolved
	Coliform
	Color
	Conductivity
	Hardness
	Heterotrophic plate count
	Iron, Dissolved
	Lithium, Dissolved
	Magnesium, Dissolved
	Manganese, Dissolved
	Nickel, Dissolved
	Nitrate, as N
	Nitrogen, Total as N
	Oil and Grease
	Petroleum hydrocarbons
	pH
	Phenols
	Potassium, Dissolved
	Radium
	Radium 226
	Radium 228
	Salt
	Scale Inhibitor
	Selenium, Dissolved
	Silver, Dissolved

CAS Number	Parameters Detected in Flowback from PA and WV Operations
	Sodium, Dissolved
	Strontium, Dissolved
	Sulfide
	Surfactants
	Total Alkalinity
	Total Dissolved Solids
	Total Kjeldahl Nitrogen
	Total Organic Carbon
	Total Suspended Solids
	Volatile Acids
	Xylenes
	Zinc, Dissolved
	Zirconium

Note that the parameters listed in Table 2-2 are based on the composition of additives used or proposed for use in New York. Table 3-1 parameters are based on analytical results of flowback from operations in Pennsylvania or West Virginia.

The information in the above table is from operations in the Marcellus Shale, but they are not from a single comprehensive study. Table 3-1 data are based on analyses performed by different laboratories; most operators provided only one sample/analysis per well, a few operators provided time-series samples for a single well; the different samples were analyzed for various parameters with some overlap of parameters. Even though the data are not strictly comparable, they provide valuable insight on the potential composition of flowback at New York operations.

### 3.4.1 Marcellus Shale Coalition Report on Flowback

Recognizing the dearth of comparable flowback information within the Marcellus Shale, the Marcellus Shale Coalition (MSC) facilitated a more rigorous study in 2009 [9]. The study:

- Gathered and analyzed flowback samples from 19 gas well sites (names A through S) in Pennsylvania or West Virginia.
- Took samples at different points in time, typically of the influent water stream, and flowback water streams 1, 5, 14 and 90 days after stimulating the well. In addition, the water supply and the fracturing fluid (referred to as Day 0) were also sampled at a few locations.
- Included both vertical and horizontal wells.
- All samples were collected by a single contractor.
- All analyses were performed by a single laboratory.
- Sought input from regulatory agencies in Pennsylvania and West Virginia.
- Most samples were analyzed for conventional parameters: metals; volatile organic compounds (VOCs); semi-volatile organic compounds (SVOCs); organochlorine pesticides; polychlorinated biphenyls (PCBs); an organophosphorus pesticide;

alcohols; glycols; and acids. The specific parameters analyzed in the MSC report are listed by class as follows:

- > 29 conventional parameters in Table 3-2
- > 59 total or dissolved metals in Table 3-3
- > 70 VOCs in Table 3-4
- > 107 SVOCs in Table 3-5
- > 20 organochlorine pesticides in Table 3-6
- > 7 PCB arochlors in Table 3-7
- > 1 organophosphorus pesticide in Table 3-8
- > 5 alcohols in Table 3-9
- > 2 glycols in Table 3-10, and
- > 4 acids in Table 3-11

**Table 3-2 - Conventional analyses in MSC Study**

Acidity	Nitrate as N	Total phosphorus
Amenable cyanide	Nitrate-nitrite	Total suspended solids
Ammonia nitrogen	Nitrite as N	Turbidity
Biochemical oxygen demand	Oil & grease (HEM)	Total cyanide
Bromide	Specific conductance	Total sulfide
Chemical oxygen demand (COD)	Sulfate	pH
Chloride	TOC	Total recoverable phenolics
Dissolved organic carbon	Total alkalinity	Sulfite
Fluoride	Total dissolved solids	MBAS (mol.wt 320)
Hardness, as CaCO <sub>3</sub>	Total Kjeldahl nitrogen	

**Table 3-3 - Total and dissolved metals analyzed in MSC Study**

Aluminum	Copper	Silver
Aluminum-dissolved	Copper-dissolved	Silver-dissolved
Antimony	Iron	Sodium
Antimony-dissolved	Iron-dissolved	Sodium-dissolved
Arsenic	Lead	Strontium
Arsenic-dissolved	Lead-dissolved	Strontium-dissolved
Barium	Lithium	Thallium
Barium-dissolved	Lithium-dissolved	Thallium-dissolved
Beryllium	Magnesium	Tin
Beryllium-dissolved	Magnesium-dissolved	Tin-dissolved
Boron	Manganese	Titanium
Boron-dissolved	Manganese-dissolved	Titanium-dissolved
Cadmium	Molybdenum	Trivalent chromium
Cadmium-dissolved	Molybdenum-dissolved	Zinc
Calcium	Nickel	Zinc-dissolved
Calcium-dissolved	Nickel-dissolved	Hexavalent chromium-dissolved
Chromium	Potassium	Hexavalent chromium
Chromium-dissolved	Potassium-dissolved	Mercury
Cobalt	Selenium	Mercury-dissolved
Cobalt-dissolved	Selenium-dissolved	

**Table 3-4 - Volatile Organic Compounds analyzed in MSC Study**

1,1,1,2-Tetrachloroethane	2-Chloroethyl vinyl ether	Ethylbenzene
1,1,1-Trichloroethane	2-Hexanone	Isopropylbenzene
1,1,2,2-Tetrachloroethane	4-Chlorotoluene	Methyl tert-butyl ether (MTBE)
1,1,2-Trichloroethane	4-Methyl-2-pentanone (MIBK)	Methylene chloride
1,1-Dichloroethane	Acetone	Naphthalene
1,1-Dichloroethene	Acrolein	n-Butylbenzene
1,1-Dichloropropene	Acrylonitrile	n-Propylbenzene
1,2,3-Trichlorobenzene	Benzene	p-Isopropyltoluene
1,2,3-Trichloropropane	Benzyl chloride	sec-Butylbenzene
1,2,4-Trichlorobenzene	Bromobenzene	Styrene
1,2,4-Trimethylbenzene	Bromodichloromethane	tert-butyl acetate
1,2-Dibromo-3-chloropropane	Bromoform	tert-Butylbenzene
1,2-Dibromoethane (EDB)	Bromomethane	Tetrachloroethene
1,2-Dichlorobenzene	Carbon disulfide	tetrahydrofuran
1,2-Dichloroethane	Carbon tetrachloride	Toluene
1,2-Dichloropropane	Chlorobenzene	trans-1,2-Dichloroethene
1,3,5-Trimethylbenzene	Chloroethane	trans-1,3-Dichloropropene
1,3-Dichlorobenzene	Chloroform	Trichloroethene
1,3-Dichloropropane	Chloromethane	Trichlorofluoromethane
1,4-Dichlorobenzene	cis-1,2-Dichloroethene	Vinyl acetate
1,4-Dioxane	cis-1,3-Dichloropropene	Vinyl chloride
1-chloro-4-trifluoromethylbenzene	Dibromochloromethane	Xylenes (total)
2,2-Dichloropropane	Dibromomethane	
2-Butanone	Dichlorodifluoromethane	

**Table 3-5 - Semi-Volatile Organics analyzed in MSC Study**

1,2,4,5-Tetrachlorobenzene	7,12-Dimethylbenz(a)anthracene	Hexachlorocyclopentadiene
1,2-Diphenylhydrazine	Acenaphthene	Hexachloroethane
1,3-Dinitrobenzene	Acenaphthylene	Hexachloropropene
1,4-Naphthoquinone	Acetophenone	Indeno(1,2,3-cd)pyrene
1-Naphthylamine	Aniline	Isodrin
2,3,4,6-Tetrachlorophenol	Aramite	Isophorone
2,3,7,8-TCDD	Benzidine	Isosafrole
2,4,5-Trichlorophenol	Benzo(a)anthracene	Methyl methanesulfonate
2,4,6-Trichlorophenol	Benzo(a)pyrene	Nitrobenzene
2,4-Dimethylphenol	Benzo(b)fluoranthene	N-Nitrosodiethylamine
2,4-Dinitrophenol	Benzo(ghi)perylene	N-Nitrosodimethylamine
2,4-Dinitrotoluene	Benzo(k)fluoranthene	N-Nitrosodi-n-butylamine
2,6-Dichlorophenol	Benzyl alcohol	N-Nitrosodi-n-propylamine
2,6-Dinitrotoluene	bis(2-Chloroethoxy)methane	N-Nitrosodiphenylamine
2-Acetylaminofluorene	bis(2-Chloroethyl) ether	N-Nitrosomethylethylamine
2-Chloronaphthalene	bis(2-Chloroisopropyl) ether	N-Nitrosomorpholine
2-Chlorophenol	bis(2-Ethylhexyl) phthalate	N-Nitrosopiperidine
2-Methylnaphthalene	Butyl benzyl phthalate	N-Nitrosopyrrolidine
2-Methylphenol	Chlorobenzilate	O,O,O-Triethyl phosphorothioate
2-Naphthylamine	Chrysene	o-Toluidine
2-Nitroaniline	Diallate	Parathion
2-Nitrophenol	Dibenz(a,h)anthracene	p-Dimethylaminoazobenzene
2-Picoline	Dibenzofuran	Pentachlorobenzene
3,3'-Dichlorobenzidine	Diethyl phthalate	Pentachloroethane
3-Methylcholanthrene	Dimethoate	Pentachloronitrobenzene
3-Methylphenol & 4-Methylphenol	Dimethyl phthalate	Pentachlorophenol
3-Nitroaniline	Di-n-butyl phthalate	Phenanthrene
4,6-Dinitro-2-methylphenol	Di-n-octyl phthalate	Phenol
4-Aminobiphenyl	Dinoseb	Phorate
4-Bromophenyl phenyl ether	Diphenylamine	Pronamide
4-Chloro-3-methylphenol	Disulfoton	Pyrene
4-Chloroaniline	Ethyl methanesulfonate	Pyridine
4-Chlorophenyl phenyl ether	Fluoranthene	Safrole
4-Nitroaniline	Fluorene	Thionazin
4-Nitrophenol	Hexachlorobenzene	Tetraethyldithiopyrophosphate
5-Nitro-o-toluidine	Hexachlorobutadiene	

**Table 3-6 - Organochlorine pesticides analyzed in MSC Study**

4,4'-DDD	delta-BHC	Endrin ketone
4,4'-DDE	Dieldrin	gamma-BHC (Lindane)
4,4'-DDT	Endosulfan I	Heptachlor
Aldrin	Endosulfan II	Heptachlor epoxide
alpha-BHC	Endosulfan sulfate	Methoxychlor
beta-BHC	Endrin	Toxaphene
Chlordane	Endrin aldehyde	



**Table 3-7 – PCBs analyzed in MSC Study**

Aroclor 1016	Aroclor 1242	Aroclor 1260
Aroclor 1221	Aroclor 1248	
Aroclor 1232	Aroclor 1254	

**Table 3-8 - Organophosphorus Pesticides analyzed in MSC Study**

Ethyl parathion
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**Table 3-9 - Alcohols analyzed in MSC Study**

2-Propanol	Ethanol	n-Propanol
Butyl alcohol	Methanol	

**Table 3-10 – Glycols analyzed in MSC Study**

Ethylene glycol
Propylene glycol

**Table 3-11 – Acids analyzed in MSC Study**

Acetic acid	Propionic acid
Butyric acid	Volatile acids

Table 3-12 is a summary of parameter classes analyzed for (shown with a “•”) at each well site. Table 3-13 is a summary of parameters detected at quantifiable levels. The check mark (√) indicates that several samples detected many parameters within a class. The MSC Study Report lists the following qualifiers associated with analytical results:

- The sample was diluted (from 1X, which means no dilution, to up to 1000X) due to concentrations of analytes exceeding calibration ranges of the instrumentation or due to potential matrix effect. The laboratory will use best judgment when analyzing samples at the lowest dilution factors allowable without causing potential damage to the instrumentation.
- The analyte was detected in the associated lab method blank for the sample. Sample results would be flagged with a laboratory-generated single letter qualifier (i.e., “B”).
- The estimated concentration of the analyte was detected between the method detection limit and the reporting limit. Sample results would be flagged with a laboratory-generated single letter qualifier (i.e., “J”). These results should be considered as estimated concentrations.
- The observed value was less than the method detection limit. These results will be flagged with a “U”.

**Table 3-12 – Parameter classes analyzed for in MSC Study**

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Conventional Analyses	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Metals	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
VOCs	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
SVOC	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Organochlorine Pesticides	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
PCBs	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Organophosphorus Pesticides	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Alcohols	NA	•	NA	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Glycols	NA	•	NA	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Acids	NA	NA	NA	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•

**Table 3-13 – Parameter classes detected in flowback analyticals in MSC Study**

	# parameters analyzed for	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Conventional Analyses	29	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√
Metals	59	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√
VOCs	70	7	6	1	2	2	6	1	5	2	2	3	7	2	1	2	7	1	5	5
SVOC	107	3	6	1	5	3	6	2	2	9	8	6	2	1	1	1	6	1	7	6
Organochlorine Pesticides	20	0	0	1	1	0	1	0	2	1	2	1	1	1	0	0	0	2	3	2
PCBs	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
Organophosphorus Pesticides	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Alcohols	5	0	1	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Glycols	2	0	1	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Acids	4	0	0	0	0	1	1	1	1	1	1	1	1	1	2	1	1	1	2	2

Metals and conventional parameters were detected and quantified in many of the samples and these observations are consistent with parameters listed in Table 3-1. However, the frequency of occurrence of other parameter classes was much lower: Table 3-13 summarizes the number of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), PCBs, pesticides, alcohols, glycols and acids observed in samples taken from each well. For the purposes of Table 3-13, if a particular parameter was detected in any sample from a single well, whether detected in one or all five (Day 0, 1, 5, 14 or 90) samples, it was considered to be one parameter.

- Between 1 and 7 of the 70 volatile organic compounds were detected in samples from well sites A through S. VOCs detected included

1,2,3-Trichlorobenzene	Benzene	Isopropylbenzene
1,2,4-Trimethylbenzene	Bromoform	Naphthalene
1,3,5-Trimethylbenzene	Carbondisulfide	Toluene
2-Butanone	Chloroform	Xylenes
Acetone	Chloromethane	
Acrylonitrile	Ethylbenzene	

- Between 1 and 9 of the 107 semi-volatile organic compounds were detected in samples from well sites A through S. SVOCs detected included

2,4-Dimethylphenol	Benzo(b)fluoranthene	Fluoranthene
2,6-Dichlorophenol	Benzo(ghi)perylene	Fluorene
2-Methylnaphthalene	Benzo(k)fluoranthene	Indeno(1,2,3-cd)pyrene
2-Methylphenol	Benzyl alcohol	N-Nitrosodiphenylamine
2-Picoline	bis(2-Chloroethyl) ether	Phenanthrene
3-Methylphenol & 4-Methylphenol	bis(2-Ethylhexyl) phthalate	Phenol
7,12-Dimethylbenz(a)anthracene	Dibenz(a,h)anthracene	Pyridine
Acetophenone	Di-n-butyl phthalate	Safrole
Benzo(a)pyrene	Diphenylamine	

- At most 3 of the 20 organochlorine pesticides were detected. Organochlorine pesticides detected included

4,4 DDE	cyclohexane (gamma BHC)	endrin aldehyde
Aldrin	endosulfan I	Heptachlor
cyclohexane (beta BHC)	endosulfan II	heptachlor epoxide

- Only 1 (Aroclor 1248) of the 7 PCBs was detected, and that from only one well site.
- Only 1 organophosphorus pesticide was analyzed for; but it was not detected in any sample.
- Of the 5 alcohols analyzed for, 2 were detected at one well site and 1 each was detected at two well sites. Alcohols that were detected are 2-propanol and methanol.

- Of the 2 glycols (ethylene glycol and propylene glycol) analyzed for, 1 each was detected at three well sites.
- Of the 4 acids analyzed for, 1 or 2 acids (acetic acid and volatile acids) were detected at several well sites.

Some parameters found in analytical results may be due to additives or supply water used in fracturing or drilling; some may be due to reactions between different additives; while others may have been mobilized from within the formation; still other parameters may have been contributed from multiple sources. Some of the volatile and semi-volatile analytical results may be traced back to potential laboratory contamination due to improper ventilation; due to chromatography column breakdown; or due to chemical breakdown of compounds during injection onto the instrumentation. Further study would be required to identify the specific origin of each parameter.

Nine pesticides and one PCB were identified by the MSC Study that were not identified by the flowback analytical results previously received from industry; all other parameters identified in the MSC study were already identified in the additives and/or flowback information received from industry.

Pesticides and PCBs do not originate within the shale play. If pesticides or PCBs were present in limited flowback samples in PA or WV, pesticides or PCBs would likely have been introduced to the shale or water during drilling or fracturing operations. Whether the pesticides or PCBs were introduced via additives or source water could not be evaluated with available information.

### **3.5 Temporal Trends in Flowback Fluids Composition**

The composition of flowback changes with time, depending on a variety of factors. Limited time-series Marcellus Shale flowback data from Pennsylvania operations, including data from the MSC Study Report, indicate that:

- The concentrations of total dissolved solids (TDS), chloride, and barium increase [7,9];
- The levels of radioactivity increase<sup>10</sup>, and sometimes exceed Maximum Contaminant Levels (MCLs) (see Table 4-2 - Primary Drinking Water Standards);
- Calcium and magnesium hardness increases;
- Iron concentrations increase, unless iron-controlling additives are used;
- Sulfate levels decrease;
- Alkalinity levels decrease, likely due to use of acid; and
- Concentrations of metals increase<sup>11</sup>.

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<sup>10</sup> Limited data from operations in PA and WV have reported the following ranges of radioactivity: alpha 22.41 – 18950 pCi/L; beta 9.68 – 7445 pCi/L; Radium<sup>226</sup> 2.58 - 33 pCi/L.

<sup>11</sup> Metals such as aluminum, antimony, arsenic, barium, boron, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, radium, selenium, silver, sodium, strontium,

Available literature [1] corroborates the above summary regarding the changes in composition with time for TDS, chlorides, and barium. Fracturing fluids pumped into the well, and mobilization of materials within the shale may be contributing to the changes seen in hardness, sulfate, and metals. The specific changes would likely depend on the shale formation, fracturing fluids used and fracture operations control.

### **3.6 Summary**

Flowback consists of fracturing fluids injected into the shale formation, new compounds that may form due to decomposition or reactions between additives, and mobilization of substances in the shale formation. The flowback rate and composition change with time. Typically, approximately 20-35 percent of fracturing fluids return to the surface over a period of approximately 2-3 weeks. Flowback from almost all shale formations appears to have high concentrations of TDS (primarily due to chlorides); flowback from the Marcellus Shale consists of high concentrations of TDS and barium, and trace amounts of several other parameters (reported in Table 3-1).

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thallium, titanium, and zinc have been reported in flowback analyses. It is important to note that not all these metals were detected in each well.

## **4 SUFFICIENCY OF REGULATIONS AND GUIDELINES**

This section summarizes existing environmental regulations and guidelines that govern the use of water associated with well drilling and hydraulic fracturing in New York State. The goal is to assess the sufficiency of these regulations and guidelines at regulating the water-related aspects of high volume hydraulic fracturing operations.

### **4.1 Background**

Water for use at the well pads may be obtained from a variety of sources including surface water, groundwater, public water supplies, and treatment system effluents. The water is trucked or pumped to the well pads and stored in tanks, pits or impoundments<sup>12</sup> until used for any of a variety of purposes including well drilling and completion, testing of pipelines, and dust control. By far, the largest use of water is for hydraulic fracturing. Hydraulic fracturing of the Marcellus Shale will require larger volumes of water to fracture the rocks than have previously been utilized in fracturing operations at other gas wells in New York. Each well may use between 0.5 and 6 million gallons of water.

As discussed in Section 2.4, hydraulic fracturing fluid typically contains additives which increase the effectiveness of the fracturing operations by ensuring that the proppant is delivered and remains in the fractures, while preventing corrosion of the well casing materials. The well must be constructed so that the fracturing fluid is only pumped into the zone targeted for fracturing.

A large portion of the fluid pumped during hydraulic fracturing remains in the shale formation (i.e., is considered consumed), but a significant portion (approximately 20 to 35 percent) normally returns to the surface as flowback and must be managed in accordance with applicable regulations. Existing well construction and fluid containment requirements are intended to prohibit any uncontrolled release of fluids to the environment.

The oil and gas industry has provided information and data to NYSDEC regarding the formulation of additives that may be used. The constituents of the fluid may then be subjected to evaluation to identify potential areas of concern where additional regulatory controls may be needed to sufficiently protect the environment.

Currently, applicants seeking permits to drill horizontal Marcellus Shale wells where high-volume hydraulic fracturing will be utilized are required to complete a site-specific Environmental Impact Statement (EIS), which must take into account the same issues being considered in the Supplemental GEIS process and must be consistent with the requirements of the State Environmental Quality Review Act and the State Environmental Conservation Law (ECL).

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<sup>12</sup> A pit is typically associated with just one well pad, whereas an impoundment infers a centralized temporary water storage location that services several well pads.

The ECL is the body of law that established NYSDEC and authorizes its programs; the State Public Health Law similarly relates to the New York State Department of Health (NYSDOH). The regulations that implement the ECL and the Public Health Law are contained in the New York Codes, Rules and Regulations (NYCRR). Of relevance to this project are the regulations contained in Title 6 - Environmental Conservation (6NYCRR), and Title 10 – Health (10NYCRR). New York environmental and health regulations draw in large measure from federal regulations that implement the Clean Water Act (CWA), the Safe Drinking Water Act (SDWA), and other legislation. A summary of the applicable regulations follows.

## **4.2 Water Use Classifications**

Surface water and groundwater sources are classified by the best type use that is or could be made of the source. The preservation of these uses is a regulatory requirement in New York. 6NYCRR Part 701 identifies and assigns the classifications of surface waters and groundwaters in New York [10].

In general, the discharge of sewage, industrial waste or other wastes may not cause impairment of the best usages of the receiving water as specified by the water classifications at the location of discharge and at other locations that may be affected by such discharge. In addition, for higher quality waters, NYSDEC may impose discharge restrictions (described below) in order to protect public health, or the quality of distinguished value or sensitive waters.

A table of water use classifications, usages, and restrictions follows [10].

**Table 4-1 - New York Water Use Classifications**

<b>Water Use Class</b>	<b>Water Type</b>	<b>Best Usages and Suitability</b>	<b>Notes</b>
N	Fresh Surface	1, 2	
AA-Special	Fresh Surface	3, 4, 5, 6	Note a
A-Special	Fresh Surface	3, 4, 5, 6	Note b
AA	Fresh Surface	3, 4, 5, 6	Note c
A	Fresh Surface	3, 4, 5, 6	Note d
B	Fresh Surface	4, 5, 6	
C	Fresh Surface	5, 6, 7	
D	Fresh Surface	5, 7, 8	
SA	Saline Surface	4, 5, 6, 9	
SB	Saline Surface	4, 5, 6,	
SC	Saline Surface	5, 6, 7	
I	Saline Surface	5, 6, 10	
SD	Saline Surface	5, 8	
GA	Fresh Groundwater	11	
GSA	Saline Groundwater	12	Note e
GSB	Saline Groundwater	13	Note f
Other – T/TS	Fresh Surface	Trout/Trout Spawning	
Other – Discharge Restriction Category	All Types	N/A	See descriptions below

Best Usage/Suitability Categories [Column 3 of Table 4-1 above]

1. Best usage for enjoyment of water in its natural condition and, where compatible, as a source of water for drinking or culinary purposes, bathing, fishing, fish propagation, and recreation
2. Suitable for shellfish and wildlife propagation and survival, and fish survival
3. Best usage as source of water supply for drinking, culinary or food processing purposes
4. Best usage for primary and secondary contact recreation
5. Best usage for fishing.
6. Suitable for fish, shellfish, and wildlife propagation and survival.
7. Suitable for primary and secondary contact recreation, although other factors may limit the use for these purposes.
8. Suitable for fish, shellfish, and wildlife survival (not propagation)
9. Best usage for shellfishing for market purposes
10. Best usage for secondary, but not primary, contact recreation
11. Best usage for potable water supply



12. Best usage for source of potable mineral waters, or conversion to fresh potable waters, or as raw material for the manufacture of sodium chloride or its derivatives or similar products
13. Best usage is as receiving water for disposal of wastes (may not be assigned to any groundwaters of the State, unless the commissioner finds that adjacent and tributary groundwaters and the best usages thereof will not be impaired by such classification)

Discharge Restriction Categories – Based on a number of relevant factors and local conditions, per 6 NYCRR 701.20, discharge restriction categories may be assigned to: (1) waters of particular public health concern; (2) significant recreational or ecological waters where the quality of the water is critical to maintaining the value for which the waters are distinguished; and (3) other sensitive waters where NYSDEC has determined that existing standards are not adequate to maintain water quality.

1. Per 6 NYCRR 701.22, new discharges may be permitted for waters where discharge restriction categories are assigned when such discharges result from environmental remediation projects, from projects correcting environmental or public health emergencies, or when such discharges result in a reduction of pollutants for the designated waters. In all cases, best usages and standards will be maintained.
2. Per 6 NYCRR 701.23, except for storm water discharges, no new discharges shall be permitted and no increase in any existing discharges shall be permitted.
3. Per 6 NYCRR 701.24, specified substance shall not be permitted in new discharges, and no increase in the release of the specified substance shall be permitted for any existing discharges. Storm water discharges are an exception to these restrictions. The substance will be specified at the time the waters are designated.

**Notes** [Column 4 of Table 4-1 above]

- a. These waters shall contain no floating solids, settleable solids, oil, sludge deposits, toxic wastes, deleterious substances, colored or other wastes or heated liquids attributable to sewage, industrial wastes or other wastes; there shall be no discharge or disposal of sewage, industrial wastes or other wastes into these waters; these waters shall contain no phosphorus and nitrogen in amounts that will result in growths of algae, weeds and slimes that will impair the waters for their best usages; there shall be no alteration to flow that will impair the waters for their best usages; there shall be no increase in turbidity that will cause a substantial visible contrast to natural conditions.
- b. This classification may be given to those international boundary waters that, if subjected to approved treatment, equal to coagulation, sedimentation, filtration and disinfection with additional treatment, if necessary, to reduce naturally present impurities, meet or will meet NYSDOH drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.
- c. This classification may be given to those waters that if subjected to pre-approved disinfection treatment, with additional treatment if necessary to remove naturally present impurities, meet or will meet NYSDOH drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.
- d. This classification may be given to those waters that, if subjected to approved treatment equal to coagulation, sedimentation, filtration and disinfection, with additional treatment if necessary to reduce naturally present impurities, meet or will meet NYSDOH drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.

- e. Class GSA waters are saline groundwaters. The best usages of these waters are as a source of potable mineral waters, or conversion to fresh potable waters, or as raw material for the manufacture of sodium chloride or its derivatives or similar products.
- f. Class GSB waters are saline groundwaters that have a chloride concentration in excess of 1,000 milligrams per liter or a total dissolved solids concentration in excess of 2,000 milligrams per liter; it shall not be assigned to any groundwaters of the State, unless the NYSDEC finds that adjacent and tributary groundwaters and the best usages thereof will not be impaired by such classification.

Water use classifications are assigned to surface waters and groundwaters throughout New York. Regulations governing gas drilling in the Marcellus Shale formation are intended to prevent the degradation of water quality that would impair the best use or suitability as assigned.

### **4.3 Drinking Water**

The protection of drinking water sources and supplies is extremely important for the maintenance of public health, and the protection of this water use type is paramount. Chemical or biological parameters that are inadvertently released into surface water or groundwater sources that are designated for drinking water use can adversely impact or disqualify such usage if there are constituents that conflict with applicable standards for drinking water. These standards are discussed below.

#### **4.3.1 Federal**

The SDWA, passed in 1974 and amended in 1986 and 1996, gives the United States Environmental Protection Agency (USEPA) the authority to set drinking water standards. There are two categories of drinking water standards: primary and secondary. Primary standards are legally enforceable and apply to public water supply systems. The secondary standards are non-enforceable guidelines that are recommended as standards for drinking water. Public water supply systems are not required to comply with secondary standards unless a state chooses to adopt them as enforceable standards. New York encourages but does not enforce the secondary standards.

The primary standards are designed to protect drinking water quality by limiting the levels of specific contaminants that can adversely affect public health and are known or anticipated to occur in drinking water. The determinations of which contaminants to regulate are based on peer-reviewed science research and data that evaluates the following factors [11]:

- Occurrence in the environment and in public water supply systems at levels of concern;
- Human exposure and risks of adverse health effects in the general population and sensitive subpopulations;
- Analytical methods of detection;

- Technical feasibility; and
- Impacts of regulation on water systems, the economy and public health.

After reviewing health effects studies and considering the risk to sensitive subpopulations, USEPA sets a non-enforceable Maximum Contaminant Level Goal (MCLG) for each contaminant as public health goals. This is the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. MCLGs only consider public health and may not be achievable given the limits of detection and best available treatment technologies. The SDWA prescribes limits in terms of Maximum Contaminant Levels (MCLs) or Treatment Techniques, which are achievable at a reasonable cost, to serve as the primary drinking water standards. A contaminant generally is classified as microbial in nature or as a carcinogenic/non-carcinogenic chemical [12].

Secondary contaminants may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. The numerical secondary standards are designed to control these effects to a level desirable to consumers [13].

Table 4-2 and Table 4-3, respectively at the end of this section, list contaminants regulated by federal primary and secondary drinking water standards [12].

In addition to the primary and secondary standards, the USEPA, on March 2, 1998, published a National Drinking Water Contaminant Candidate List (CCL), which lists contaminants that are [14]:

- Not already regulated under SDWA, but nevertheless may have adverse health effects;
- Are known or anticipated to occur in public water systems; and
- May require regulations under SDWA.

Contaminants on the CCL are prioritized and studied, including monitoring for presence/level of selected contaminants<sup>13</sup> in selected existing larger public water supply systems. If, after the requisite studies and monitoring are completed, the USEPA determines regulations are necessary, then the USEPA proceeds with drafting them. Every five years, USEPA will repeat the cycle of revising the CCL, making regulatory determinations for contaminants and identifying contaminants for unregulated monitoring. In addition, every six years, USEPA will re-evaluate existing regulations to determine if modifications are necessary [15].

In most cases, the USEPA delegates responsibility for implementing drinking water standards to the states.

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<sup>13</sup> Most of the unregulated contaminants with potential of occurring in drinking water are pesticides and microbes.

### 4.3.2 New York State

In New York, a state with delegated authority in this area, drinking water is addressed in Article 15, Title 15 of the ECL and administered by the NYSDEC via implementing regulations contained in Part 601 of 6NYCRR.

Anyone planning to operate or operating a public water supply system must obtain a Water Supply Permit from NYSDEC before undertaking any of the regulated activities.

Contact with NYSDEC and submission of a Water Supply Permit application will automatically involve the NYSDOH. The NYSDOH has a regulatory role in water quality and other sanitary aspects of a project relating to human health. Through the State Sanitary Code (Chapter 1 of 10NYCRR), the NYSDOH oversees the suitability of water for human consumption. Section 5-1.30 of 10 NYCRR prescribes the required treatment for public water systems, which at a minimum includes filtration and disinfection. To assure the safety of drinking water in New York, NYSDOH, in cooperation with its partners, the county health departments, regulates the operation, design and quality of public water supplies; assures water sources are adequately protected, and sets standards for constructing individual water supplies.

The NYSDOH regulates contaminants consistent with the national drinking water standards. Section 5-1.51 of 10 NYCRR prescribes the maximum contaminant levels, maximum residual disinfectant levels and treatment technique requirements, which are listed in section 5-1.52 tables 1 through 7 of 10 NYCRR. These tables replicate the national primary and secondary standards and CCL.

In addition, in 1988, for drinking water NYSDOH adopted the 0.005 mg/L MCL for organic chemicals belonging to any of six major chemical classes called Principal Organic Contaminant (POC)<sup>14</sup>; 0.05 mg/L MCL for Unspecified Organic Contaminant (UOC)<sup>15</sup>; and 0.1 mg/L MCL for Total POCs and UOCs. This means that publicly supplied drinking water cannot have more than 0.005 mg/L of any chemical defined as a POC; or more than 0.05 mg/L of a chemical not already covered by other regulations (UOC); or more than 0.1 mg/L of POCs and UOCs combined.

A comparison of constituents contained in hydraulic fracturing fluids, including those reported in the MSC Study, and the contaminants listed in Table 4-2, Table 4-3 and Table 4-4 is provided in Table 4-5. Nine pesticides and one PCB were identified by the MSC Study

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<sup>14</sup> The New York State Register dated November 23, 1988, Volume X, Issue 47, lists the POC classes as halogenated alkanes; halogenated ethers; halobenzenes and substituted halobenzenes; benzene and alkyl – or nitrogen-substituted benzenes; substituted, unsaturated aliphatic hydrocarbons; and halogenated non-aromatic cyclic hydrocarbons. The specific contaminants to be analyzed for under POCs are listed in Table 9D - Organic Chemicals – POCs of 10 NYCRR Subpart 5-1, and replicated in Table 4-4 herein.

<sup>15</sup> Defined as any organic chemical not covered by another MCL.

that were not previously identified by the flowback analytical results received from industry; all other parameters identified in the MSC study were already identified in the information received from industry.

It should be noted that the Federal Energy Policy Act of 2005 amended the Underground Injection Control (UIC) provisions of the SDWA to exclude hydraulic fracturing from the definition of "underground injection." The Fracturing Responsibility and Awareness of Chemicals (FRAC) Act bill presently in Congress, if passed, will subject hydraulic fracturing to regulation under the SDWA.

The objective of the federal UIC program is to protect underground sources of drinking water from contamination by underground injection of hazardous and non-hazardous fluids. Whether or not hydraulic fracturing is regulated under SDWA UIC, protection of groundwater resources during oil and gas extraction activities is a responsibility of state government, and the cited federal amendment does not diminish the NYSDEC's authority over oil and gas well development in New York, including oversight of hydraulic fracturing activities to ensure protection of potable groundwater resources.

#### **4.4 Discharge Limits – SPDES**

The direct or indirect discharge of flowback that includes residuals from additives is subject to regulation under New York's State Pollutant Discharge Elimination System (SPDES). Limitations on discharges from point sources, which are derived from federal, regional, and state standards and programs, are imposed in New York via the SPDES permit program. The USEPA has approved New York's program for the control of wastewater and stormwater discharges in accordance with the Clean Water Act (CWA). Under New York State law, the SPDES program is broader in scope than the CWA in that it controls point source discharges to groundwaters as well as surface waters. Discharges related to gas drilling activities are subject to these controls.

Applicable water quality standards and effluent limitations are those State and Federal water quality standards and effluent limitations to which a discharge is subject under the CWA or State law, including but not limited to water quality standards, effluent limitations, best management practices, standards of performance, toxic effluent standards and prohibitions, pretreatment standards, and ocean discharge criteria.

Per 6 NYCRR Section 750-1.3, certain discharges are absolutely prohibited, including any radiological, chemical or biological warfare agent or high-level radioactive waste, any obstruction to anchorage or navigation, and other highly objectionable, conflicting or non-compliant discharges.

Subsection (a) of 6 NYCRR Section 750-1.11 covers the provisions of SPDES permits and lists the citations for the various effluent limitations from the Federal Register (FR) and the Code of Federal Regulations (CFR). NYSDEC is responsible to administer these applicable effluent limitations and other requirements in the SPDES permits, whenever applicable, as

required by the CWA and as may be promulgated by the NYSDEC. These include the following:

- (1) Best Practicable Control Technology currently available (BPT) effluent limitations under Section 301 of the CWA and 40 CFR Parts 120, 125, 133 and 405-471, inclusive, (see section 750-1.24 of this Part);
- (2) Best Conventional Pollutant Control Technology (BCT) new source performance standards (NSPS), and other new source performance standards under Section 306 of the CWA and 40 CFR Parts 122.29, 129 and 405-471, inclusive (see section 750-1.24 of this Part);
- (3) Best Available Technology (BAT) effluent limitation guidelines, effluent prohibitions, and pretreatment standards for existing sources under Section 307 of the CWA and 40 CFR Parts 129 and 405-471, inclusive (see section 750-1.24 of this Part);
- (4) Ocean discharge criteria adopted by the Federal government pursuant to Section 403 of the CWA and 40 CFR Part 125, sections 125.120 - 125.124 (see section 750-1.24 of this Part);
- (5) Any more stringent limitations, including those:
  - (i) Necessary to meet water quality standards, guidance values, effluent limitations or schedules of compliance, established pursuant to any state law or regulation consistent with Section 510 of the CWA, or the requirements of 40 CFR Part 132 (see section 750-1.24 of this Part);
  - (ii) Necessary to implement a total maximum daily load/waste load allocation/load allocation established pursuant to Section 303(d) of the CWA and 40 CFR Part 130.7 (see section 750-1.24 of this Part); or
  - (iii) Necessary to meet any other State or Federal law or regulation;
- (6) Any more stringent requirements necessary to comply with a plan approved pursuant to Section 208(b) of the CWA and 40 CFR Part 35 (see section 750-1.24 of this Part);
- (7) Prior to promulgation by the administrator of applicable effluent standards and limitations, BPT effluent limitations and such conditions as the commissioner determines are necessary to carry out the provisions of this Part pursuant to Section 402 of the CWA and 40 CFR Part 125 (see section 750-1.24 of this Part).
- (8) As provided in Section 402(g) of the CWA (see section 750-1.24 of this Part), if the SPDES permit is for the discharge of pollutants into the navigable waters of the State from a vessel or other floating craft, any applicable regulations promulgated by the U.S. Department of Commerce, establishing specifications for safe transportation, handling, carriage, storage, and stowage of pollutants.
- (9) Unless otherwise required or authorized by this Part, the provisions or requirements of 40 CFR. 122.23 Concentrated animal feeding operations, 40 CFR. Part 122.24 -

Concentrated aquatic animal production facilities, 40 CFR Part 122.25 - Aquaculture projects, 40 CFR Parts 122.26, 122.30 to 122.37, and 122.42(c) & (d) - Storm Water Discharges, 40 CFR Part 122.27 - Silvicultural activities (applicable to SPDES), 40 CFR Part 122.44 - Establishing limitations, standards, and other permit conditions, 40 CFR Part 122.45 - Calculating NPDES permit conditions, 40 CFR Part 125 - Criteria and Standards for NPDES, 40 CFR Part 133 - Secondary Treatment Regulation, 40 CFR Part 401 - General Provisions and 40 CFR Part 403 - General Pretreatment Regulations, except 40 CFR Part 403.10 (see section 750-1.24 of this Part).

(10) 40 CFR 122.50 (see section 750-1.24 of this Part).

(11) The requirements or provisions of this Part.

Subsection (b) of 6NYCRR Section 750-1.11 covers industrial waste discharges into publicly owned treatment works, which must comply with toxic effluent limitations and pretreatment standards and with monitoring, reporting, recording, sampling and entry requirements provided by Section 307 of the CWA and 40 CFR Parts 129 and 405-471, inclusive; and Section 308 of the CWA and 40 CFR Parts 122 and 125 (see section 750-1.24 of this Part); or ECL Article 17, or adopted pursuant to ECL Article 17 of this Title.

The SPDES permit application requires any applicant to provide analytical results for several classes of pollutants listed in the following tables:

Table 6 - Priority Pollutants;

Table 7 - Other Significant Pollutants with NYSDEC Standards/Guidance Values and USEPA/NYSDEC Promulgated Analytical Methods;

Table 8 - Other Significant Pollutants with USEPA/NYSDEC Promulgated Analytical Methods;

Table 9 - Other Significant Pollutants with NYSDEC Standards/Guidance Values; and

Table 10 - Other Pollutants and Hazardous Substances Required to be Identified in ICS by Applicants if Present at Facility in Significant Levels.

#### **4.5 Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations**

Included in the above discussion are those rules and regulations that establish standards that generally apply to industrial activities, but that also have applicability to the oil, gas, and solution mining industrial category. In addition, a guidance value may be used where a standard for a substance or group of substances has not been established for a particular water class and type of value [16].

Division of Water Technical and Operational Guidance Series 1.1.1 (TOGS111) - Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations is a compilation of ambient water quality guidance values and groundwater effluent limitations for use where there are no standards (in 6 NYCRR 703.5) or regulatory effluent limitations (in 6 NYCRR 703.6).

## **4.6 Lists of Chemicals in Additives and Flowback Addressed in NY Regulations or Guidances**

Table 4-5, at the end of this section, lists chemical constituents of additives and parameters found in a limited number of analytical samples of flowback fluids received via NYSDEC. Columns 5-9 of Table 4-5 indicate if any of these chemicals/parameters are regulated by the federal primary or secondary drinking water standards, covered in Tables 6-10 of the SPDES program, or in Table 1 or 5 of TOGS111.

Table 4-6 lists parameters found in limited flowback analyses from PA and WV that are regulated in NY; this table does not include results from the MSC Study. Column 3 is the number of samples that analyzed for the particular parameter; column 4 is the number in which the parameter was detected. Columns 5, 6 and 7 provide the minimum, median and maximum concentrations detected.

Table 4-7 lists parameters found in limited flowback analyses from PA and WV that appear not to be regulated in NY. Column 2 is the number of samples that analyzed for the particular parameter; column 3 is the number in which the parameter was detected. Basic statistics for these parameters are in subsequent columns. Given the limited number of analyses performed on these parameters, the results and statistics should be used with caution.

## **4.7 Rules and Regulations Applicable to Oil, Gas, and Solution Mining Category**

### **4.7.1 Federal**

40 CFR Part 435 provides guidelines on effluent limitations for the Oil and Gas Extraction Point Source Category. These guidelines are taken into consideration when the permitting authority develops discharge permit limitations for a point source discharger in this category. Subpart C of 40 CFR 435 specifically applies to facilities engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry that are located on land (i.e., excludes offshore and coastal locations).

The applicable limits in this subcategory reflect BPT: there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment (*i.e.*, produced water, drilling muds, drill cuttings, and produced sand).

### **4.7.2 New York State**

NYSDEC's Division of Mineral Resources administers regulations and a permitting program to mitigate to the greatest extent possible any potential environmental impact of gas drilling and well operation.



6 NYCCR Part 554 addresses drilling practices applicable to oil, gas, and solution salt mining activities. Subpart 554.1 prescribes requirements for pollution and migration prevention. These requirements include:

- The prevention of pollution associated with the drilling, casing and completion program adopted for any well.
- A prohibition on pollution of the land and/or of fresh surface water or fresh groundwater resulting from exploration or drilling.
- Prior to the issuance of a well-drilling permit for any operation in which the potential exists that brine, salt water or other polluting fluids will be produced or obtained during drilling operations in sufficient quantities to be deleterious to the surrounding environment, the need for the operator to submit and receive approval of a plan for the environmentally safe and proper ultimate disposal of such fluids (excluding drilling muds, which, as specified by regulation, are not considered to be polluting fluids for the purposes of 6 NYCRR 554.1(c)(1)).
  - Depending on the method of disposal chosen by the applicant, a permit for discharge and/or disposal may be required by the NYSDEC in addition to the well-drilling permit.
  - An applicant may also be required to submit an acceptable contingency plan, the use of which shall be required if the primary plan is unsafe or impracticable at the time of disposal.
- A prohibition on the impounding of brine or salt water in an earthen pit where the soil underlying the pit is porous and/or is closely underlaid by a gravel, rock or sand stratum unless the pit is lined with watertight material.
  - Brine or salt water may be temporarily stored prior to disposal in any watertight tank, container or an earthen pit, if underlaid by soil such as heavy clay or hardpan.
  - The tank, container or earthen pit must be constructed and maintained so as to prevent escape of any fluids, including any amounts that may be added by natural precipitation.
  - Storage of brine, salt water or other polluting fluids in such watertight tanks or earthen pits, prior to disposal, is limited to a maximum of 45 days after cessation of drilling operations, unless NYSDEC approves an extension.
- The installation of surface casing in all wells to a depth below the deepest potable fresh water level.
  - The drilling, casing and completion program adopted for any well must be such as to:

- Prevent the migration of oil, gas or other fluids from one pool or stratum to another; and
  - Exclude oil, gas or other fluids from any underground mining properties or rights and to protect them in accordance with prudent operations.
- ECL23-0305(8)(d) provides authority to NYSDEC to require the operator to remedy any contamination of a water supply well, and ECL 71-1307 provides authority to direct a violator to “reclaim and repair” any impairment to a water supply well.

The regulation summarized above is supplemented by required casing and cementing practices, enforced as permit conditions on each drilling permit. Surface casing must extend at least 75 feet beyond the deepest fresh water zone, or 75 feet into competent rock, whichever is deeper [17]. In primary and principal aquifers, surface casing must be set at least 100 feet below the deepest fresh water zone and at least 100 feet into bedrock. Additionally, as stated in the GEIS (p. 9-32), although the cited regulations do mention clay and hardpan as options in pit construction, NYSDEC has consistently required plastic liners in all temporary earthen drilling pits [18].

#### **4.8 Other Agencies and Activities with Jurisdiction**

New York State is a member of compacts established to regulate and protect important interstate water resources. These include the Susquehanna River Basin Commission, the Delaware River Basin Commission, and the Great Lakes Commission.

In addition, New York has specific programs, plans, and procedures in place that are focused on maintaining or improving ambient water quality in targeted watersheds. These include total maximum daily loads, and state or local watershed management or protection plans.

Although these commissions, programs, plans, and procedures carry the force of law, they are specific to individual water bodies or watersheds and, therefore, are not included in this review.

The Emergency Planning and Community Right-to-Know Act (EPCRA) applies to the manufacturing sector, including the oil and gas industry (although not oil or gas conveyance pipelines). In addition, existing well construction and fluid containment requirements sufficiently prohibit any uncontrolled release of fluids to the environment. Also, well permit Applicants are required to submit information on hydraulic fracturing fluid composition prior to well permit issuance, subject to regulations that protect information identified by Applicants as trade secret or confidential commercial information.

Additional environmental laws exist to address other activities related to gas well drilling in the New York Marcellus Shale area. These include the Resource Conservation and Recovery Act (RCRA) regarding hazardous waste, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regarding toxic substances, and the Clean Air Act (CAA) regarding emissions. A review of the federal and New York regulations that

implement these laws and their applicability to the oil and gas industry is beyond the scope of this review.

#### **4.9 Conclusions**

This section provides a summary of federal and New York State environmental regulations and guidelines that apply to gas well drilling and extraction in the New York portion of Marcellus Shale region related to water use. They are intended to address concerns that the oil and gas industry may not be fully subject to certain key provisions of the SWDA, CWA, and other water resource-related environmental laws.

This review provides information regarding the sufficiency of regulatory controls in place in New York to protect specified water uses, including drinking water sources, from drilling activities, injection of fluids for hydraulic fracturing, and management of flowback or brines that flow back to surface during well development or operation. These controls are implemented in the permitting process for well drilling and completion; for point source discharges via the SPDES program; and where there are no standards or regulatory effluent limitations, via Technical & Operational Guidance Series 1.1.1 (TOGS111). In addition, drinking water supplies are protected by Federal Drinking Water Standards, and NYSDOH's POC and UOC standards. Except for those parameters listed in Table 4-7, all parameters detected in flowback analyticals that were provided by industry via NYSDEC, including parameters detected in the MSC Study, are presently addressed by existing Federal or State regulations or guidances.

**Table 4-2 - Primary Drinking Water Standards**

<b>Microorganisms</b>	<b>Contaminant</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
	Cryptosporidium	0	TT
	Giardia lamblia	0	TT
	Heterotrophic plate count	n/a	TT
	Legionella	0	TT
	Total Coliforms (including fecal coliform and E. coli)	0	5%
	Turbidity	n/a	TT
	Viruses (enteric)	0	TT

MCLG: Maximum contaminant level goal

MCL: Maximum contaminant level

TT: Treatment technology

<b>Disinfection Byproducts</b>	<b>Contaminant</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
	Bromate	0	0.01
	Chlorite	0.8	1
	Haloacetic acids (HAA5)	n/a	0.06
	Total Trihalomethanes (TTHMs)	n/a	0.08

<b>Disinfectants</b>	<b>Contaminant</b>	<b>MRDLG (mg/L)</b>	<b>MRDL (mg/L)</b>
	Chloramines (as Cl <sub>2</sub> )	4.0	4.0
	Chlorine (as Cl <sub>2</sub> )	4.0	4.0
	Chlorine dioxide (as ClO <sub>2</sub> )	0.8	0.8

MRDL: Maximum Residual Disinfectant Level

MRDLG: Maximum Residual Disinfectant Level Goal

<b>Inorganic Chemicals</b>	<b>Contaminant</b>	<b>CAS number</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
	Antimony	07440-36-0	0.006	0.006
	Arsenic	07440-38-2	0	0.01 as of 01/23/06
	Asbestos (fiber >10 micrometers)	01332-21-5	7 million fibers per liter	7 MFL
	Barium	07440-39-3	2	2
	Beryllium	07440-41-7	0.004	0.004
	Cadmium	07440-43-9	0.005	0.005
	Chromium (total)	07440-47-3	0.1	0.1
	Copper	07440-50-8	1.3	TT; Action Level=1.3
	Cyanide (as free cyanide)	00057-12-5	0.2	0.2
	Fluoride	16984-48-8	4	4
	Lead	07439-92-1	0	TT; Action Level=0.015

**Inorganic  
Chemicals**

<b>Contaminant</b>	<b>CAS number</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
Mercury (inorganic)	07439-97-6	0.002	0.002
Nitrate (measured as Nitrogen)		10	10
Nitrite (measured as Nitrogen)		1	1
Selenium	07782-49-2	0.05	0.05
Thallium	07440-28-0	0.0005	0.002

**Organic  
Chemicals**

<b>Contaminant</b>	<b>CAS number</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
Acrylamide	00079-06-1	0	TT
Alachlor	15972-60-8	0	0.002
Atrazine	01912-24-9	0.003	0.003
Benzene	00071-43-2	0	0.005
Benzo(a)pyrene (PAHs)	00050-32-8	0	0.0002
Carbofuran	01563-66-2	0.04	0.04
Carbon tetrachloride	00056-23-5	0	0.005
Chlordane	00057-74-9	0	0.002
Chlorobenzene	00108-907	0.1	0.1
2,4-Dichloro-phenoxyacetic acid (2,4-D)	00094-75-7	0.07	0.07
Dalapon	00075-99-0	0.2	0.2
1,2-Dibromo-3- chloropropane (DBCP)	00096-12-8	0	0.0002
o-Dichlorobenzene	00095-50-1	0.6	0.6
p-Dichlorobenzene	00106-46-7	0.075	0.075
1,2-Dichloroethane	00107-06-2	0	0.005
1,1-Dichloroethylene	00075-35-4	0.007	0.007
cis-1,2-Dichloroethylene	00156-59-2	0.07	0.07
trans-1,2-Dichloroethylene	00156-60-5	0.1	0.1
Dichloromethane	00074-87-3	0	0.005
1,2-Dichloropropane	00078-87-5	0	0.005
Di(2-ethylhexyl) adipate	00103-23-1	0.4	0.4
Di(2-ethylhexyl) phthalate	00117-81-7	0	0.006
Dinoseb	00088-85-7	0.007	0.007
Dioxin (2,3,7,8-TCDD)	01746-01-6	0	0.00000003
Diquat		0.02	0.02
Endothall	00145-73-3	0.1	0.1
Endrin	00072-20-8	0.002	0.002
Epichlorohydrin		0	TT
Ethylbenzene	00100-41-4	0.7	0.7
Ethylene dibromide	00106-93-4	0	0.00005
Glyphosate	01071-83-6	0.7	0.7
Heptachlor	00076-44-8	0	0.0004
Heptachlor epoxide	01024-57-3	0	0.0002
Hexachlorobenzene	00118-74-1	0	0.001
Hexachlorocyclopentadiene	00077-47-4	0.05	0.05

**Organic  
Chemicals**

<b>Contaminant</b>	<b>CAS number</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
Lindane	00058-89-9	0.0002	0.0002
Methoxychlor	00072-43-5	0.04	0.04
Oxamyl (Vydate)	23135-22-0	0.2	0.2
Polychlorinated biphenyls (PCBs)		0	0.0005
Pentachlorophenol	00087-86-5	0	0.001
Picloram	01918-02-1	0.5	0.5
Simazine	00122-34-9	0.004	0.004
Styrene	00100-42-5	0.1	0.1
Tetrachloroethylene	00127-18-4	0	0.005
Toluene	00108-88-3	1	1
Toxaphene	08001-35-2	0	0.003
2,4,5-TP (Silvex)	00093-72-1	0.05	0.05
1,2,4-Trichlorobenzene	00120-82-1	0.07	0.07
1,1,1-Trichloroethane	00071-55-6	0.2	0.2
1,1,2-Trichloroethane	00079-00-5	0.003	0.005
Trichloroethylene	00079-01-6	0	0.005
Vinyl chloride	00075-01-4	0	0.002
Xylenes (total)		10	10

**Radionuclides**

<b>Contaminant</b>	<b>MCLG (mg/L)</b>	<b>MCL or TT (mg/L)</b>
Alpha particles	none ----- zero	15 picocuries per Liter (pCi/L)
Beta particles and photon emitters	none ----- zero	4 millirems per year
Radium 226 and Radium 228 (combined)	none ----- zero	5 pCi/L
Uranium	zero	30 ug/L

**Table 4-3 - Secondary Drinking Water Standards**

Contaminant	CAS number	Standard
Aluminum	07439-90-5	0.05 to 0.2 mg/L
Chloride		250 mg/L
Color		15 (color units)
Copper	07440-50-8	1.0 mg/L
Corrosivity		noncorrosive
Fluoride	16984-48-8	2.0 mg/L
Foaming Agents (surfactants)		0.5 mg/L
Iron	07439-89-6	0.3 mg/L
Manganese	07439-96-5	0.05 mg/L
Odor		3 threshold odor number
pH		6.5-8.5
Silver	07440-22-4	0.10 mg/L
Sulfate	14808-79-8	250 mg/L
Total Dissolved Solids		500 mg/L
Zinc	07440-66-6	5 mg/L

**Table 4-4 – Specific Contaminants included within NYSDOH POCs Standards<sup>a,b</sup>**

Contaminant	Standard (mg/L)
1,1,1,2-Tetrachloroethane	0.005
1,1,1-Trichloroethane	0.005
1,1,2,2-Tetrachloroethane	0.005
1,1,2-Trichloroethane	0.005
1,1-Dichloroethane	0.005
1,1-Dichloroethene	0.005
1,1-Dichloropropene	0.005
1,2,3-Trichlorobenzene	0.005
1,2,3-Trichloropropane	0.005
1,2,4-Trichlorobenzene	0.005
1,2,4-Trimethylbenzene	0.005
1,2-Dichlorobenzene	0.005
1,2-Dichloroethane	0.005
1,2-Dichloropropane	0.005
1,3,5-Trimethylbenzene	0.005
1,3-Dichlorobenzene	0.005
1,3-Dichloropropane	0.005
1,4-Dichlorobenzene	0.005
2,2-Dichloropropane	0.005
2-Chlorotoluene	0.005
4-Chlorotoluene	0.005

<b>Contaminant</b>	<b>Standard (mg/L)</b>
Benzene	0.005
Bromobenzene	0.005
Bromochloromethane	0.005
Bromomethane	0.005
Carbon Tetrachloride	0.005
Chlorobenzene	0.005
Chloroethane	0.005
Chloromethane	0.005
cis-1,2-Dichloroethene	0.005
cis-1,3-Dichloropropene	0.005
Dibromomethane	0.005
Dichlorodifluoromethane	0.005
Ethylbenzene	0.005
Hexachlorobutadiene	0.005
Isopropylbenzene	0.005
Methylene Chloride	0.005
m-Xylene	0.005
N-Butylbenzene	0.005
n-Propylbenzene	0.005
o-Xylene	0.005
p-Isopropyltoluene	0.005
p-Xylene	0.005
Sec-Butylbenzene	0.005
Styrene	0.005
Tert-Butylbenzene	0.005
Tetrachloroethene	0.005
Toluene	0.005
trans-1,2-Dichloroethene	0.005
Trans-1,3-Dichloropropene	0.005
Trichloroethene	0.005
Trichlorofluoromethane	0.005

a Per 10 NYCRR Subpart 5-1 the MCL for each UOC (which are organic chemicals that are not covered by another MCL) is 0.05 mg/L.

b Per 10 NYCRR Subpart 5-1 the MCL total POCs and UOCs is 0.1 mg/L.



**Table 4-5 – Comparison of additives used or proposed for use in NY, parameters detected in analytical results of flowback from the Marcellus operations in PA and WV<sup>16</sup>, and parameters regulated via primary and secondary drinking water standards, SPDES Program or listed in TOGS111**

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
106-24-1	(2E)-3,7-dimethylocta-2,6-dien-1-ol	Yes						§
67701-10-4	(C8-C18) And (C18) Unsaturated Alkylcarboxylic Acid Sodium Salt	Yes						§§
02634-33-5	1,2-Benzisothiazolin-2-one / 1,2-benzisothiazolin-3-one	Yes						§
00087-61-6	1,2,3-Trichlorobenzene		Yes			Table 9	Tables 1,5	POC
00095-63-6	1,2,4 trimethylbenzene	Yes	Yes			Table 9	Tables 1,5	POC
93858-78-7	1,2,4-Butanetricarboxylicacid, 2-phosphono-, potassium salt	Yes						§
00108-67-8	1,3,5-Trimethylbenzene		Yes			Tables 9,10	Tables 1,5	POC

<sup>16</sup> This table includes parameters detected in the MSC Study.

<sup>17</sup> As with Table 2-2, information in the “Used in Additives” column is based on the composition of additives used or proposed for use in New York.

<sup>18</sup> Parameters marked with (¥) indicates that the compound dissociates, and its components are separately regulated. Not all dissociating compounds are marked.

<sup>19</sup> As with Table 3-1, information in the “Found in Flowback” column is based on analytical results of flowback from operations in Pennsylvania or West Virginia. There are/may be products used in fracturing operations in Pennsylvania that have not yet been proposed for use in New York for which, therefore, the NYSDEC does not have chemical composition data.

<sup>20</sup> Limits marked with a pound sign (#) are based on secondary drinking water standards.

<sup>21</sup> SPDES or TOGS typically regulates or provides guidance for the total substance, e.g. iron; and rarely regulates or provides guidance for only its dissolved portion, e.g. dissolved iron. The dissolved component is implicitly covered in the total substance. Therefore, the dissolved component is not included in Table 4-5. Flowback analyses provided information for the total and dissolved components of metals, which are listed in Table 3-1 and in Table 4-6. Understanding the dissolved vs. suspended portions of a substance is valuable when determining potential treatment techniques.

<sup>22</sup> Cells marked with a section sign (§) indicates that if the parameter is not already covered by any other applicable regulation which provides an MCL, 10 NYCRR applies the default UOC MCL of 0.05 mg/L for each parameter, or 0.1 mg/L for the total POCs and UOCs. Double signs (§§) indicate that the free compound would be UOC, but that salts would not be UOC.

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
00123-91-1	1,4 Dioxane	Yes				Table 8		§
03452-07-1	1-eicosene	Yes						§
00629-73-2	1-hexadecene	Yes						§
104-46-1	1-Methoxy-4-propenylbenzene	Yes						§
124-28-7	1-Octadecanamine, N, N-dimethyl- / N,N-Timethyloctadecylamine	Yes						§
112-03-8	1-Octadecanaminium, N,N,N-Trimethyl-, Chloride / Trimethyloctadecylammonium chloride	Yes						§
00112-88-9	1-octadecene	Yes						§
40623-73-2	1-Propanesulfonic acid	Yes						§
01120-36-1	1-tetradecene	Yes						§
98-55-5	2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol	Yes						§
10222-01-2	2,2 Dibromo-3-nitrilopropionamide	Yes				Table 9	Tables 1,5	
27776-21-2	2,2'-azobis-{2-(imidazlin-2-yl)propane}-dihydrochloride	Yes						§
73003-80-2	2,2-Dobromomalonamide	Yes						§
00105-67-9	2,4-Dimethylphenol		Yes			Table 6	Tables 1,5	
00087-65-0	2,6-Dichlorophenol		Yes			Table 8		
15214-89-8	2-Acrylamido-2-methylpropanesulphonic acid sodium salt polymer	Yes						§
46830-22-2	2-acryloyloxyethyl(benzyl)dimethylammonium chloride	Yes						§
00052-51-7	2-Bromo-2-nitro-1,3-propanediol	Yes				Table 10		
00111-76-2	2-Butoxy ethanol /Ethylene glycol monobutyl ether / Butyl Cellusolve	Yes						§
01113-55-9	2-Dibromo-3-Nitrilopropionamide / 2-Monobromo-3-nitrilopropionamide	Yes						§
00104-76-7	2-Ethyl Hexanol	Yes						§
00091-57-6	2-Methylnaphthalene		Yes			Table 8	Tables 1,3	
00095-48-7	2-Methylphenol		Yes			Table 8		
109-06-8	2-Picoline (2-methyl pyridine)		Yes			Table 8	Table 3	
00067-63-0	2-Propanol / Isopropyl Alcohol / Isopropanol / Propan-2-ol	Yes	Yes			Table 10		

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
26062-79-3	2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-chloride, homopolymer	Yes						§
95077-68-2	2-Propenoic acid, homopolymer sodium salt	Yes						§
09003-03-6	2-propenoic acid, homopolymer, ammonium salt	Yes						§
25987-30-8	2-Propenoic acid, polymer with 2 p-propenamide, sodium salt / Copolymer of acrylamide and sodium acrylate	Yes						§
71050-62-9	2-Propenoic acid, polymer with sodium phosphinate (1:1)	Yes						§
66019-18-9	2-propenoic acid, telomer with sodium hydrogen sulfite	Yes						§
00107-19-7	2-Propyn-1-ol / Progargyl Alcohol	Yes						§
51229-78-8	3,5,7-Triaza-1-azoniatricyclo[3.3.1.1 <sup>3,7</sup> ]decane, 1-(3-chloro-2-propenyl)-chloride,	Yes						§
106-22-9	3,7 - dimethyl-6-octen-1-ol	Yes						§
5392-40-5	3,7-dimethyl-2,6-octadienal	Yes						POC
00115-19-5	3-methyl-1-butyn-3-ol	Yes						§
00108-39-4	3-Methylphenol		Yes			Table 8		
104-55-2	3-phenyl-2-propenal	Yes						POC
127-41-3	4-(2,6,6-trimethyl-1-cyclohex-2-enyl)-3-buten-2-one	Yes						§
00072-55-9	4,4 DDE		Yes			Table 6	Tables 1,5	
121-33-5	4-hydroxy-3-methoxybenzaldehyde	Yes						§
00106-44-5	4-Methylphenol		Yes			Table 8		
127087-87-0	4-Nonylphenol Polyethylene Glycol Ether Branched / Nonylphenol ethoxylated / Oxyalkylated Phenol	Yes						§
00057-97-6	7,12-Dimethylbenz(a)anthracene		Yes			Table 8	Table 3	
00064-19-7	Acetic acid	Yes	Yes			Table 10		
68442-62-6	Acetic acid, hydroxy-, reaction products with triethanolamine	Yes						§
00108-24-7	Acetic Anhydride	Yes				Table 10		

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
00067-64-1	Acetone	Yes	Yes			Table 7	Tables 1,5	
00098-86-2	Acetophenone		Yes				Table 3	
00079-06-1	Acrylamide	Yes		0	TT	Table 9	Tables 1,5	
38193-60-1	Acrylamide - sodium 2-acrylamido-2-methylpropane sulfonate copolymer	Yes						§
25085-02-3	Acrylamide - Sodium Acrylate Copolymer or Anionic Polyacrylamide	Yes						§
69418-26-4	Acrylamide polymer with N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride	Yes						§
15085-02-3	Acrylamide-sodium acrylate copolymer	Yes						§
00107-13-1	Acrylonitrile		Yes			Table 6	Tables 1,5	
68891-29-2	Alcohols C8-10, ethoxylated, monoether with sulfuric acid, ammonium salt	Yes						§§
68526-86-3	Alcohols, C11-14-iso-, C13-rich	Yes						§
68551-12-2	Alcohols, C12-C16, Ethoxylated (a.k.a. Ethoxylated alcohol)	Yes						§
00309-00-2	Aldrin		Yes				Tables 1,5	
	Aliphatic acids	Yes						§
	Aliphatic alcohol glycol ether	Yes						§
64742-47-8	Aliphatic Hydrocarbon / Hydrotreated light distillate / Petroleum Distillates / Isoparaffinic Solvent / Paraffin Solvent / Napthenic Solvent	Yes						§
	Alkalinity, Carbonate, as CaCO3		Yes			Table 10		
64743-02-8	Alkenes	Yes						§
68439-57-6	Alkyl (C14-C16) olefin sulfonate, sodium salt	Yes						§
	Alkyl Aryl Polyethoxy Ethanol	Yes						§
	Alkylaryl Sulfonate	Yes						§
09016-45-9	Alkylphenol ethoxylate surfactants	Yes		0.5 mg/L <sup>#</sup>				
	Alpha, Radiation		Yes	none ----- 0	15 picocuries per Liter (pCi/L)	Table 7	Tables 1,5	

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
07439-90-5	Aluminum		Yes	0.05 to 0.2 mg/L <sup>#</sup>		Table 7	Tables 1,5	
01327-41-9	Aluminum chloride	Yes (¥)						
68155-07-7	Amides, C8-18 and C19-Unsatd., N,N-Bis(hydroxyethyl)	Yes						
73138-27-9	Amines, C12-14-tert-alkyl, ethoxylated	Yes						§
71011-04-6	Amines, Ditalow alkyl, ethoxylated	Yes						§
68551-33-7	Amines, tallow alkyl, ethoxylated, acetates	Yes						§
01336-21-6	Ammonia	Yes				Yes		
00631-61-8	Ammonium acetate	Yes				Table 10		
68037-05-8	Ammonium Alcohol Ether Sulfate	Yes (¥)						§
07783-20-2	Ammonium bisulfate	Yes (¥)						
10192-30-0	Ammonium Bisulphite	Yes (¥)						
12125-02-9	Ammonium Chloride	Yes (¥)				Table 10		
07632-50-0	Ammonium citrate	Yes (¥)						
37475-88-0	Ammonium Cumene Sulfonate	Yes (¥)						
01341-49-7	Ammonium hydrogen-difluoride	Yes (¥)						
06484-52-2	Ammonium nitrate	Yes (¥)						
07727-54-0	Ammonium Persulfate / Diammonium peroxidisulphate	Yes (¥)						
01762-95-4	Ammonium Thiocyanate	Yes				Table 10		
	Anionic copolymer	Yes						
07440-36-0	Antimony		Yes	0.006	0.006	Table 6	Tables 1,5	
07664-41-7	Aqueous ammonia	Yes	Yes			Table 7	Tables 1,5	
12672-29-6	Aroclor 1248		Yes			Table 6		
	Aromatic hydrocarbons	Yes						§
	Aromatic ketones	Yes						§
07440-38-2	Arsenic		Yes	0	0.01	Table 6	Tables 1,5	
12174-11-7	Attapulgite Clay	Yes						
07440-39-3	Barium		Yes	2	2	Table 7	Tables 1,5	
	Barium Strontium P.S. (mg/L)		Yes					

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex / organophilic clay	Yes						§
00071-43-2	Benzene	Yes	Yes	0	0.005	Table 6	Tables 1,5	POC
119345-04-9	Benzene, 1,1'-oxybis, tetrapropylene derivatives, sulfonated, sodium salts	Yes						§
74153-51-8	Benzenemethanaminium, N,N-dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-, chloride, polymer with 2-propenamide	Yes						§
122-91-8	Benzenemethanol,4-methoxy-, 1-formate	Yes						§
1300-72-7	Benzenesulfonic acid, Dimethyl-, Sodium salt (aka Sodium xylene sulfonate)	Yes						§
00050-32-8	Benzo(a)pyrene		Yes			Table 6		
00205-99-2	Benzo(b)fluoranthene		Yes				Tables 1,5	
00191-24-2	Benzo(ghi)perylene		Yes			Table 6	Table 3	
00207-08-9	Benzo(k)fluoranthene		Yes			Table 6	Tables 1,5	
140-11-4	Benzyl acetate	Yes						§
00100-51-6	Benzyl alcohol		Yes			Table 8	Table 3	
07440-41-7	Beryllium		Yes	0.004	0.004	Table 6	Tables 1,5	
	Beta, Radiation		Yes	none ----- 0	4 millirems per year	Table 7	Tables 1,5	
	Bicarbonates (mg/L)		Yes			Table 10		
76-22-2	Bicyclo (2.2.1) heptan-2-one, 1,7,7-trimethyl-	Yes						§
	Biochemical Oxygen Demand		Yes			Yes		
00111-44-4	Bis(2-Chloroethyl) ether		Yes			Table 6	Tables 1,5	
00117-81-7	Bis(2-ethylhexyl)phthalate / Di(2-ethylhexyl)phthalate		Yes	0	0.006	Table 6	Tables 1,5	
68153-72-0	Blown lard oil amine	Yes						
68876-82-4	Blown rapeseed amine	Yes						
1319-33-1	Borate Salt	Yes						
10043-35-3	Boric acid	Yes						

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
01303-86-2	Boric oxide / Boric Anhydride	Yes						
07440-42-8	Boron		Yes			Table 7	Tables 1,5	
24959-67-9	Bromide		Yes			Table 7	Tables 1,5	
00075-25-2	Bromoform		Yes			Table 6	Tables 1,5	
00071-36-3	Butan-1-ol	Yes				Table 10	Tables 1,5	
68002-97-1	C10 - C16 Ethoxylated Alcohol	Yes						§
68131-39-5	C12-15 Alcohol, Ethoxylated	Yes						§
07440-43-9	Cadmium		Yes	0.005	0.005	Table 6	Tables 1,5	
07440-70-2	Calcium		Yes			Table 8		
1317-65-3	Calcium Carbonate	Yes				Table 10		
10043-52-4	Calcium chloride	Yes (¥)						
1305-62-0	Calcium Hydroxide	Yes						
1305-79-9	Calcium Peroxide	Yes						
00124-38-9	Carbon Dioxide	Yes	Yes					
00075-15-0	Carbondisulfide		Yes			Table 8	Tables 1,5	
68130-15-4	Carboxymethylhydroxypropyl guar	Yes						§
09012-54-8	Cellulase / Hemicellulase Enzyme	Yes						§
09004-34-6	Cellulose	Yes						§
	Cesium 137		Yes		Via beta radiation			
	Chemical Oxygen Demand		Yes			Yes		
	Chloride		Yes	250 mg/L <sup>#</sup>		Table 7	Tables 1,5	
10049-04-4	Chlorine Dioxide	Yes		MRDLG = 0.8	MRDL=0.8	Table 10		
00124-48-1	Chlorodibromomethane		Yes			Table 6	Tables 1,5	
00067-66-3	Chloroform		Yes			Table 6	Tables 1,5	
78-73-9	Choline Bicarbonate	Yes						§§
67-48-1	Choline Chloride	Yes						§§
91-64-5	Chromen-2-one	Yes						§
07440-47-3	Chromium		Yes	0.1	0.1	Table 6	Tables 1,5	
00077-92-9	Citric Acid	Yes						§
94266-47-4	Citrus Terpenes	Yes						§

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
07440-48-4	Cobalt		Yes			Table 7	Table 1	
61789-40-0	Cocamidopropyl Betaine	Yes						§
68155-09-9	Cocamidopropylamine Oxide	Yes						§
68424-94-2	Coco-betaine	Yes						§
	Coliform, Total		Yes	0	0.05	Table 7		
	Color		Yes	15 (Color Units) <sup>#</sup>		Table 7		
07440-50-8	Copper		Yes	1.0 <sup>#</sup>	TT; Action Level=1.3	Table 6	Tables 1,5	
07758-98-7	Copper (II) Sulfate	Yes (¥)						
14808-60-7	Crystalline Silica (Quartz)	Yes			Via solids and TSS			
07447-39-4	Cupric chloride dihydrate	Yes (¥)						
00057-12-5	Cyanide		Yes	0.2	0.2	Table 6	Tables 1,5	
00319-85-7	Cyclohexane (beta BHC)		Yes			Table 6	Tables 1,5	
00058-89-9	Cyclohexane (gamma BHC)		Yes	0.0002	0.0002	Table 6	Tables 1,5	
1490-04-6	Cyclohexanol,5-methyl-2-(1-methylethyl)	Yes						§
8007-02-1	Cymbopogon citratus leaf oil	Yes						
8000-29-1	Cymbopogon winterianus jowitt oil	Yes						
01120-24-7	Decyldimethyl Amine	Yes (¥)						§
02605-79-0	Decyl-dimethyl Amine Oxide	Yes (¥)						§
00055-70-3	Dibenz(a,h)anthracene		Yes				Table 3	
03252-43-5	Dibromoacetonitrile	Yes				Table 9	Tables 1	
00075-27-4	Dichlorobromomethane		Yes			Table 6	Tables 1,5	
25340-17-4	Diethylbenzene	Yes						§
00111-46-6	Diethylene Glycol	Yes				Table 10		
22042-96-2	Diethylenetriamine penta (methylenephonic acid) sodium salt	Yes						§
28757-00-8	Diisopropyl naphthalenesulfonic acid	Yes						§
68607-28-3	Dimethylcocoamine, bis(chloroethyl) ether, diquatary ammonium salt	Yes						§



CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
07398-69-8	Dimethyldiallylammonium chloride	Yes						§
00084-74-2	Di-n-butyl phthalate		Yes			Table 6	Tables 1,5	
00122-39-4	Diphenylamine		Yes			Table 7	Tables 1,5	
25265-71-8	Dipropylene glycol	Yes						§
34590-94-8	Dipropylene glycol methyl ether	Yes						§
00139-33-3	Disodium Ethylene Diamine Tetra Acetate	Yes						§
64741-77-1	Distillates, petroleum, light hydrocracked	Yes						
05989-27-5	D-Limonene	Yes						§
00123-01-3	Dodecylbenzene	Yes						§
27176-87-0	Dodecylbenzene sulfonic acid	Yes						§
42504-46-1	Dodecylbenzenesulfonate isopropanolamine	Yes						§
00050-70-4	D-Sorbitol / Sorbitol	Yes						§
37288-54-3	Endo-1,4-beta-mannanase, or Hemicellulase	Yes						§
00959-98-8	Endosulfan I		Yes			Table 6	Table 3	
33213-65-9	Endosulfan II		Yes			Table 6	Table 3	
07421-93-4	Endrin aldehyde		Yes			Table 6	Tables 1,5	
149879-98-1	Erucic Amidopropyl Dimethyl Betaine	Yes						§
00089-65-6	Erythorbic acid, anhydrous	Yes						§
54076-97-0	Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride, homopolymer	Yes						§
00107-21-1	Ethane-1,2-diol / Ethylene Glycol	Yes	Yes			Table 7	Tables 1,5	
111-42-2	Ethanol, 2,2-iminobis-	Yes						§
26027-38-3	Ethoxylated 4-nonylphenol	Yes						
09002-93-1	Ethoxylated 4-tert-octylphenol	Yes						§
68439-50-9	Ethoxylated alcohol	Yes						§
126950-60-5	Ethoxylated alcohol	Yes						§
68951-67-7	Ethoxylated alcohol (C14-15)	Yes						§
68439-46-3	Ethoxylated alcohol (C9-11)	Yes						§
66455-15-0	Ethoxylated Alcohols	Yes						§
67254-71-1	Ethoxylated Alcohols (C10-12)	Yes						§
84133-50-6	Ethoxylated Alcohols (C12-14 Secondary)	Yes						§

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
68439-51-0	Ethoxylated Alcohols (C12-14)	Yes						§
78330-21-9	Ethoxylated branch alcohol	Yes						§
34398-01-1	Ethoxylated C11 alcohol	Yes						§
78330-21-8	Ethoxylated C11-14-iso, C13-rich alcohols	Yes						§
61791-12-6	Ethoxylated Castor Oil	Yes						§
61791-29-5	Ethoxylated fatty acid, coco	Yes						§
61791-08-0	Ethoxylated fatty acid, coco, reaction product with ethanolamine	Yes						
68439-45-2	Ethoxylated hexanol	Yes						§
09036-19-5	Ethoxylated octylphenol	Yes						§
09005-67-8	Ethoxylated Sorbitan Monostearate	Yes						§
09005-70-3	Ethoxylated Sorbitan Trioleate	Yes						§
118-61-6	Ethyl 2-hydroxybenzoate	Yes						§
00064-17-5	Ethyl alcohol / ethanol	Yes						
00100-41-4	Ethyl Benzene	Yes	Yes	0.7	0.7	Table 6	Tables 1,5	POC
93-89-0	Ethyl benzoate	Yes						§
00097-64-3	Ethyl Lactate	Yes						§
09003-11-6	Ethylene Glycol-Propylene Glycol Copolymer (Oxirane, methyl-, polymer with oxirane)	Yes						§
00075-21-8	Ethylene oxide	Yes				Table 9	Tables 1,5	
05877-42-9	Ethyl octynol	Yes						§
8000-48-4	Eucalyptus globulus leaf oil	Yes						
61790-12-3	Fatty Acids	Yes						§
68604-35-3	Fatty acids, C 8-18 and C18-unsaturated compounds with diethanolamine	Yes						
68188-40-9	Fatty acids, tall oil reaction products w/ acetophenone, formaldehyde & thiourea	Yes						
09043-30-5	Fatty alcohol polyglycol ether surfactant	Yes		0.5 mg/L <sup>#</sup>				§
07705-08-0	Ferric chloride	Yes				Table 10		
07782-63-0	Ferrous sulfate, heptahydrate	Yes						
00206-44-0	Fluoranthene		Yes			Table 6	Tables 1,5	
00086-73-7	Fluorene		Yes			Table 6	Tables 1,5	

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
16984-48-8	Fluoride		Yes	2 <sup>#</sup>	4	Table 7	Tables 1,5	
00050-00-0	Formaldehyde	Yes				Table 8	Tables 1,5	
29316-47-0	Formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane	Yes						§
153795-76-7	Formaldehyde, polymers with branched 4-nonylphenol, ethylene oxide and propylene oxide	Yes						§
00075-12-7	Formamide	Yes						§
00064-18-6	Formic acid	Yes				Table 10		
00110-17-8	Fumaric acid	Yes				Table 10		
65997-17-3	Glassy calcium magnesium phosphate	Yes						
00111-30-8	Glutaraldehyde	Yes						§
00056-81-5	Glycerol / glycerine	Yes						§
09000-30-0	Guar Gum	Yes						§
64742-94-5	Heavy aromatic petroleum naphtha	Yes						§
09025-56-3	Hemicellulase	Yes						§
00076-44-8	Heptachlor		Yes	0	0.0002		Tables 1,5	
01024-57-3	Heptachlor epoxide		Yes	0	0.0002		Tables 1,5	
	Heterotrophic plate count		Yes	n/a	TT <sup>23</sup>			
07647-01-0	Hydrochloric Acid / Hydrogen Chloride / muriatic acid	Yes						
07722-84-1	Hydrogen Peroxide	Yes				Table 10		
64742-52-5	Hydrotreated heavy naphthenic distillate	Yes						
00079-14-1	Hydroxy acetic acid	Yes						§
35249-89-9	Hydroxyacetic acid ammonium salt	Yes						§
09004-62-0	Hydroxyethyl cellulose	Yes						§
05470-11-1	Hydroxylamine hydrochloride	Yes						§
39421-75-5	Hydroxypropyl guar	Yes						§
00193-39-5	Indeno(1,2,3-cd)pyrene		Yes			Table 6	Tables 1,5	

<sup>23</sup> Treatment Technology specified.

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
07439-89-6	Iron		Yes	0.3 mg/L <sup>#</sup>		Table 7	Tables 1,5	
35674-56-7	Isomeric Aromatic Ammonium Salt	Yes						§
64742-88-7	Isoparaffinic Petroleum Hydrocarbons, Synthetic	Yes						§
00064-63-0	Isopropanol	Yes				Table 10		
00098-82-8	Isopropylbenzene (cumene)	Yes	Yes			Table 9	Tables 1,5	POC
68909-80-8	Isoquinoline, reaction products with benzyl chloride and quinoline	Yes						§
08008-20-6	Kerosene	Yes						
64742-81-0	Kerosine, hydrodesulfurized	Yes						
00063-42-3	Lactose	Yes						
8022-15-9	Lavandula hybrida abrial herb oil	Yes						
07439-92-1	Lead		Yes	0	TT; Action Level 0.015	Table 6	Tables 1,5	
64742-95-6	Light aromatic solvent naphtha	Yes						§
01120-21-4	Light Paraffin Oil	Yes						§
	Lithium		Yes			Table 10		
07439-95-4	Magnesium		Yes			Table 7	Tables 1,5	
546-93-0	Magnesium Carbonate	Yes						
1309-48-4	Magnesium Oxide	Yes						
1335-26-8	Magnesium Peroxide	Yes						
14807-96-6	Magnesium Silicate Hydrate (Talc)	Yes						
07439-96-5	Manganese		Yes	0.05 mg/L <sup>#</sup>		Table 7	Tables 1,5	
07439-97-6	Mercury		Yes	0.002	0.002	Table 6	Tables 1,5	
01184-78-7	Methanamine, N,N-dimethyl-, N-oxide	Yes						§
00067-56-1	Methanol	Yes	Yes			Table 10		
119-36-8	Methyl 2-hydroxybenzoate	Yes						§
00074-83-9	Methyl Bromide		Yes			Table 6	Tables 1,5	POC
00074-87-3	Methyl Chloride / chloromethane		Yes	0	0.005	Table 6	Tables 1,5	POC
00078-93-3	Methyl ethyl ketone / 2-Butanone		Yes			Table 7	Tables 1,5	

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
68891-11-2	Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched	Yes						§
08052-41-3	Mineral spirits / Stoddard Solvent	Yes						
64742-46-7	Mixture of severely hydrotreated and hydrocracked base oil	Yes						
07439-98-7	Molybdenum		Yes			Table 7		
00141-43-5	Monoethanolamine	Yes						§
44992-01-0	N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride	Yes						§
64742-48-9	Naphtha (petroleum), hydrotreated heavy	Yes						§
00091-20-3	Naphthalene	Yes	Yes			Table 6	Tables 1,5	
38640-62-9	Naphthalene bis(1-methylethyl)	Yes						§
00093-18-5	Naphthalene, 2-ethoxy-	Yes						§
68909-18-2	N-benzyl-alkyl-pyridinium chloride	Yes						§
68139-30-0	N-Cocoamidopropyl-N,N-dimethyl-N-2-hydroxypropylsulfobetaine	Yes						§
07440-02-0	Nickel		Yes			Table 6	Tables 1,5	
	Nitrate, as N		Yes	10	10	Table 7	Tables 1,5	
07727-37-9	Nitrogen, Liquid form	Yes						
	Nitrogen, Total as N		Yes				Table 5	
00086-30-6	N-Nitrosodiphenylamine		Yes			Table 6	Tables 1,5	
26027-38-3	Nonylphenol Ethoxylate	Yes						
68412-54-4	Nonylphenol Polyethoxylate	Yes						§
	Oil and Grease		Yes				Table 5	
8000-27-9	Oils, cedarwood	Yes						
121888-66-2	Organophilic Clays	Yes						
	Oxyalkylated alkylphenol	Yes						§
628-63-7	Pentyl acetate	Yes						§
540-18-1	Pentyl butanoate	Yes						§
8009-03-8	Petrolatum	Yes						
64742-65-0	Petroleum Base Oil	Yes						§

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
	Petroleum distillate blend	Yes						§
64742-52-5	Petroleum Distillates	Yes						
	Petroleum hydrocarbons		Yes					§
64741-68-0	Petroleum naphtha	Yes						§
	pH		Yes	6.5-8.5 <sup>#</sup>			Table 5	
00085-01-8	Phenanthrene		Yes			Table 6	Tables 1,5	
00108-95-2	Phenol		Yes			Table 6	Tables 1,5	
	Phenols		Yes			Table 6	Tables 1,5	
101-84-8	Phenoxybenzene	Yes						§
70714-66-8	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt	Yes						
57723-14-0	Phosphorus		Yes			Table 7	Table 1	
08000-41-7	Pine Oil	Yes						
8002-09-3	Pine oils	Yes						
60828-78-6	Poly(oxy-1,2-ethanediyl), a-[3,5-dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-	Yes						§
25322-68-3	Poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy / Polyethylene Glycol	Yes						§
24938-91-8	Poly(oxy-1,2-ethanediyl), α-tridecyl- ω-hydroxy	Yes						§
31726-34-8	Poly(oxy-1,2-ethanediyl),alpha-hexyl-omega-hydroxy	Yes						
9004-32-4	Polyanionic Cellulose	Yes						
51838-31-4	Polyepichlorohydrin, trimethylamine quaternized	Yes						§
56449-46-8	polyethylene glycol oleate ester	Yes						§
	Polyethoxylated alkanol	Yes						§
9046-01-9	Polyethoxylated tridecyl ether phosphate	Yes						§
63428-86-4	Polyethylene glycol hexyl ether sulfate, ammonium salt	Yes						§

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
62649-23-4	Polymer with 2-propenoic acid and sodium 2-propenoate	Yes						§
	Polymeric Hydrocarbons	Yes						§
09005-65-6	Polyoxyethylene Sorbitan Monooleate	Yes						§
61791-26-2	Polyoxylated fatty amine salt	Yes						§
65997-18-4	Polyphosphate	Yes						
07440-09-7	Potassium		Yes			Table 8		
00127-08-2	Potassium acetate	Yes						
1332-77-0	Potassium borate	Yes						
12712-38-8	Potassium borate	Yes						
20786-60-1	Potassium borate	Yes						
00584-08-7	Potassium carbonate	Yes						
07447-40-7	Potassium chloride	Yes						
00590-29-4	Potassium formate	Yes						
01310-58-3	Potassium Hydroxide	Yes				Table 10		
13709-94-9	Potassium metaborate	Yes						
24634-61-5	Potassium Sorbate	Yes						
112926-00-8	Precipitated silica / silica gel	Yes						
00057-55-6	Propane-1,2-diol, or Propylene glycol	Yes	Yes			Table 10	Table 3 <sup>24</sup>	
00057-55-6	Propylene glycol							
00107-98-2	Propylene glycol monomethyl ether	Yes				Table 10		
00110-86-1	Pyridine		Yes			Table 7	Tables 1,5	
68953-58-2	Quaternary Ammonium Compounds	Yes				Table 9	Tables 1	
62763-89-7	Quinoline,2-methyl-, hydrochloride	Yes						
15619-48-4	Quinolinium, 1-(phenylmethyl),chloride	Yes						
	Radium		Yes			Table 7		

<sup>24</sup> TOGS lists this parameter as CAS 58-55-6.

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
	Radium 226		Yes	none ----- zero	5 pCi/L	Table 7	Tables 1,5	
	Radium 228		Yes	none ----- zero	5 pCi/L		Tables 1,5	
8000-25-7	Rosmarinus officinalis l. leaf oil	Yes						
00094-59-7	Safrole		Yes			Table 8	Table 3	
	Salt of amine-carbonyl condensate	Yes						
	Salt of fatty acid/polyamine reaction product	Yes						
	Scale Inhibitor (mg/L)		Yes					§
07782-49-2	Selenium		Yes	0.05	0.05	Table 6	Tables 1,5	
07631-86-9	Silica, Dissolved	Yes				Table 8		
07440-22-4	Silver		Yes	0.10 mg/L <sup>#</sup>		Table 6	Tables 1,5	
07440-23-5	Sodium		Yes			Table 7	Tables 1,5	
05324-84-5	Sodium 1-octanesulfonate	Yes						
00127-09-3	Sodium acetate	Yes						
95371-16-7	Sodium Alpha-olefin Sulfonate	Yes						
00532-32-1	Sodium Benzoate	Yes						
00144-55-8	Sodium bicarbonate	Yes						
07631-90-5	Sodium bisulfate	Yes						
07647-15-6	Sodium Bromide	Yes						
00497-19-8	Sodium carbonate	Yes						
07647-14-5	Sodium Chloride	Yes						
07758-19-2	Sodium chlorite	Yes						
03926-62-3	Sodium Chloroacetate	Yes						
00068-04-2	Sodium citrate	Yes						
06381-77-7	Sodium erythorbate / isoascorbic acid, sodium salt	Yes						
02836-32-0	Sodium Glycolate	Yes						
1301-73-2	Sodium hydroxide	Yes						
01310-73-2	Sodium Hydroxide	Yes				Table 10		



CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
07681-52-9	Sodium hypochlorite	Yes				Table 10		
07775-19-1	Sodium Metaborate .8H2O	Yes						
10486-00-7	Sodium perborate tetrahydrate	Yes						
07775-27-1	Sodium persulphate	Yes						
68608-26-4	Sodium petroleum sulfonate	Yes						
09003-04-7	Sodium polyacrylate	Yes						
07757-82-6	Sodium sulfate	Yes				Table 10		
01303-96-4	Sodium tetraborate decahydrate	Yes						
07772-98-7	Sodium Thiosulfate	Yes						
01338-43-8	Sorbitan Monooleate	Yes						
	Specific Conductivity		Yes					
07440-24-6	Strontium		Yes			Table 9	Table 1	
00057-50-1	Sucrose	Yes						
	Sugar	Yes						
05329-14-6	Sulfamic acid	Yes						
14808-79-8	Sulfate		Yes	250 mg/L <sup>#</sup>		Table 7	Tables 1,5	
	Sulfide		Yes			Table 7	Tables 1,5	
14265-45-3	Sulfite		Yes			Table 7	Table 1	
	Surfactant blend	Yes		0.5 mg/L <sup>#</sup>				
68442-77-3	Surfactant: Modified Amine	Yes						
	Surfactants MBAS		Yes	0.5 mg/L <sup>#</sup>				
112945-52-5	Synthetic Amorphous / Pyrogenic Silica / Amorphous Silica	Yes						
68155-20-4	Tall Oil Fatty Acid Diethanolamine	Yes						
08052-48-0	Tallow fatty acids sodium salt	Yes						
72480-70-7	Tar bases, quinoline derivs., benzyl chloride-quaternized	Yes						
68647-72-3	Terpene and terpenoids	Yes						§
68956-56-9	Terpene hydrocarbon byproducts	Yes						
00127-18-4	Tetrachloroethylene		Yes	0	0.005	Table 6	Tables 1,5	POC
00533-74-4	Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione / Dazomet	Yes						

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
55566-30-8	Tetrakis(hydroxymethyl)phosphonium sulfate (THPS)	Yes						
00075-57-0	Tetramethyl ammonium chloride	Yes						§
00064-02-8	Tetrasodium Ethylenediaminetetraacetate	Yes						§
07440-28-0	Thallium		Yes	0.0005	0.002	Table 6	Tables 1,5	
00068-11-1	Thioglycolic acid	Yes						
00062-56-6	Thiourea	Yes				Table 10		
68527-49-1	Thiourea, polymer with formaldehyde and 1-phenylethanone	Yes						
68917-35-1	Thuja plicata donn ex. D. don leaf oil	Yes						
07440-32-6	Titanium		Yes			Table 7		
00108-88-3	Toluene	Yes	Yes	1	1	Table 6	Tables 1,5	POC
	Total Dissolved Solids		Yes	500 mg/L <sup>#</sup>			Table 5	
	Total Kjeldahl Nitrogen		Yes			Yes		
	Total Organic Carbon		Yes			Yes		
	Total Suspended Solids		Yes			Yes		
81741-28-8	Tributyl tetradecyl phosphonium chloride	Yes						
	Triethanolamine	Yes						§
68299-02-5	Triethanolamine hydroxyacetate	Yes						
00112-27-6	Triethylene Glycol	Yes						§
52624-57-4	Trimethylolpropane, Ethoxylated, Propoxylated	Yes						§
00150-38-9	Trisodium Ethylenediaminetetraacetate	Yes						§
05064-31-3	Trisodium Nitrilotriacetate	Yes						§
07601-54-9	Trisodium ortho phosphate	Yes						
00057-13-6	Urea	Yes						
07440-62-2	Vanadium		Yes			Table 7	Table 1	
25038-72-6	Vinylidene Chloride/Methylacrylate Copolymer	Yes						

CAS Number	Parameter Name	Used in Additives <sup>17, 18</sup>	Found in Flowback <sup>19</sup>	MCLG (mg/L) <sup>20</sup>	MCL or TT (mg/L)	SPDES Tables <sup>21</sup>	TOGS111 Tables	POC / UOC <sup>22</sup>
	Volatile Acids		Yes			<sup>25</sup>		
7732-18-5	Water	Yes						
8042-47-5	White Mineral Oil	Yes						
11138-66-2	Xanthan gum	Yes						
	Xylenes	Yes	Yes	10	10		Table 1,5	POC
13601-19-9	Yellow Sodium of Prussiate	Yes						
07440-66-6	Zinc		Yes	5 mg/L <sup>#</sup>		Table 6	Tables 1,5	
	Zirconium		Yes					

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<sup>25</sup> Several volatile compounds regulated via SPDES Table 6. Need to evaluate constituents.

**Table 4-6 – Typical concentrations of flowback constituents based on limited samples from PA and WV, and regulated in NY<sup>26, 27</sup>**

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
00067-64-1	Acetone	3	1	681	681	681	µg/L
	Acidity, Total	4	4	101	240	874	mg/L
	Alkalinity <sup>28</sup>	155	155	0	153	384	mg/L
	Alkalinity, Carbonate, as CaCO <sub>3</sub>	164	163	0	9485	48336	mg/L
	Total Alkalinity	5	5	28	91	94	mg/L
	Alpha, Radiation	15	15	0	166	18950	pCi/L
07439-90-5	Aluminum	43	12	0.02	0.07	1.2	mg/L
	Aluminum, Dissolved	22	1	1.37	1.37	1.37	mg/L
07440-36-0	Antimony	34	1	0.26	0.26	0.26	mg/L
07664-41-7	Aqueous ammonia	48	45	11.3	44.8	382	mg/L
07440-38-2	Arsenic	43	7	0.015	0.09	0.123	mg/L
07440-39-3	Barium	48	47	0.553	1450	15700	mg/L
	Barium, Dissolved	22	22	0.313	212	19200	mg/L
00071-43-2	Benzene	35	14	15.7	479.5	1950	µg/L
07440-41-7	Beryllium	43	1	422	422	422	mg/L
	Beta, Radiation	15	15	0	62	7445	pCi/L

<sup>26</sup> Information presented in Table 4-6 and Table 4-7 is based on limited data from Pennsylvania and West Virginia. Characteristics of flowback from the Marcellus Shale in New York are expected to be similar to flowback from Pennsylvania and West Virginia, but not identical. In addition, the raw data for these tables came from several sources, with likely varying degrees of reliability. Also, the analytical methods used were not all the same for given parameters. Sometimes laboratories need to use different analytical methods depending on the consistency and quality of the sample; sometimes the laboratories are only required to provide a certain level of accuracy. Therefore, the method detection limits may be different. The quality and composition of flowback from a single well can also change within a few days soon after the well is fractured. This data does not control for any of these variables. Additionally, it should be noted that several of these compounds could be traced back to potential laboratory contamination. Further comparisons of analytical results with those results from associated laboratory method blanks may be required to further assess the extent of actual concentrations found in field samples versus elevated concentrations found in field samples due to blank contamination.

<sup>27</sup> This table does not include results from the MSC Study.

<sup>28</sup> Different data sources reported alkalinity in different and valid forms. Total alkalinity reported here is smaller than carbonate alkalinity because the data came from different sources.

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
	Bicarbonates	150	150	0	183	1708	mg/L
	Biochemical Oxygen Demand	38	37	3	200	4450	mg/L
00117-81-7	Bis(2-ethylhexyl)phthalate	20	2	10.3	15.9	21.5	µg/L
07440-42-8	Boron	23	9	0.539	2.06	26.8	mg/L
24959-67-9	Bromide	15	15	11.3	607	3070	mg/L
00075-25-2	Bromoform	26	2	34.8	36.65	38.5	µg/L
07440-43-9	Cadmium	43	6	0.007	0.025	1.2	mg/L
	Cadmium, Dissolved	22	2	0.017	0.026	0.035	mg/L
07440-70-2	Calcium	187	186	29.9	4241	123000	mg/L
	Calcium, Dissolved	3	3	2360	22300	31500	mg/L
	Cesium 137 <sup>29</sup>	16	2	9.9	10.2	10.5	pCi/L
	Chemical Oxygen Demand	38	38	223	5645	33300	mg/L
	Chloride	193	193	287	56900	228000	mg/L
00124-48-1	Chlorodibromomethane	26	2	3.28	3.67	4.06	µg/L
07440-47-3	Chromium	43	9	0.009	0.082	760	mg/L
	Chromium (VI), dissolved	19	10	0.0126	0.539	7.81	mg/L
	Chromium, Dissolved	22	2	0.058	0.075	0.092	mg/L
07440-48-4	Cobalt	30	6	0.03	0.3975	0.62	mg/L
	Cobalt, dissolved	19	1	0.489	0.489	0.489	mg/L
	Coliform, Total	5	2	1	42	83	Col/100mL
	Color	3	3	200	1000	1250	PCU
07440-50-8	Copper	43	8	0.01	0.0245	0.157	mg/L
00057-12-5	Cyanide	7	2	0.006	0.0125	0.019	mg/L
00075-27-4	Dichlorobromomethane	29	1	2.24	2.24	2.24	µg/L
00100-41-4	Ethyl Benzene	38	14	3.3	53.6	164	µg/L
16984-48-8	Fluoride	4	2	5.23	392.615	780	mg/L
	Heterotrophic plate count	5	3	25	50	565	CFU/mL
07439-89-6	Iron	193	168	0	29.2	810	mg/L
	Iron, Dissolved	34	26	6.75	63.25	196	mg/L
07439-92-1	Lead	43	6	0.008	0.035	27.4	mg/L

<sup>29</sup> Regulated under beta particles [19].

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
	Lithium	13	13	34.4	90.4	297	mg/L
	Lithium, Dissolved	4	4	24.5	61.35	144	mg/L
07439-95-4	Magnesium	193	180	9	177	3190	mg/L
	Magnesium, Dissolved	3	3	218	2170	3160	mg/L
	Mg as CaCO3	145	145	36	547	8208	mg/L
07439-96-5	Manganese	43	29	0.15	1.89	97.6	mg/L
	Manganese, Dissolved	22	12	0.401	2.975	18	mg/L
07439-97-6	Mercury	30	2	0.0006	0.295	0.59	mg/L
00074-83-9	Methyl Bromide	26	1	2.04	2.04	2.04	µg/L
00074-87-3	Methyl Chloride	26	1	15.6	15.6	15.6	µg/L
07439-98-7	Molybdenum	34	12	0.16	0.44	1.08	mg/L
00091-20-3	Naphthalene	23	1	11.3	11.3	11.3	µg/L
07440-02-0	Nickel	43	15	0.01	0.03	0.137	mg/L
	Nickel, Dissolved	22	2	0.03	0.0715	0.113	mg/L
	Nitrate, as N	1	1	0.025	0.025	0.025	mg/L
	Nitrogen, Total as N	1	1	13.4	13.4	13.4	mg/L
	Oil and Grease	39	9	5	17	1470	mg/L
	Petroleum hydrocarbons	1	1	0.21	0.21	0.21	mg/L
	pH	191	191	0	6.6	8.58	S.U.
00108-95-2	Phenol	20	1	459	459	459	µg/L
	Phenols	35	5	0.05	0.191	0.44	mg/L
57723-14-0	Phosphorus, as P	3	3	0.89	1.85	4.46	mg/L
07440-09-7	Potassium	33	17	15.5	125	7810	mg/L
	Potassium, Dissolved	3	3	84.2	327	7080	mg/L
	Radium	6	3	7.7	9.7	24	pCi/L
	Radium 226	3	3	2.58	4.67	33	pCi/L
	Radium 228	3	3	1.15	4.66	18.41	pCi/L
	Scale Inhibitor	145	145	315	744	1346	mg/L
07782-49-2	Selenium	34	1	0.058	0.058	0.058	mg/L
	Selenium, Dissolved	22	1	1.06	1.06	1.06	mg/L
07440-22-4	Silver	43	3	0.129	0.204	6.3	mg/L
	Silver, Dissolved	22	2	0.056	0.0825	0.109	mg/L
07440-23-5	Sodium	42	41	83.1	23500	96700	mg/L
	Sodium, Dissolved	3	3	9290	54800	77400	mg/L

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
07440-24-6	Strontium	36	36	0.501	1115	5841	mg/L
	Strontium, Dissolved	22	21	8.47	629	7290	mg/L
14808-79-8	Sulfate (as SO <sub>4</sub> )	193	169	0	1	1270	mg/L
	Sulfide (as S)	8	1	29.5	29.5	29.5	mg/L
14265-45-3	Sulfite (as SO <sub>3</sub> )	3	3	2.56	64	64	mg/L
	Surfactants <sup>30</sup>	12	12	0.1	0.21	0.61	mg/L
00127-18-4	Tetrachloroethylene	26	1	5.01	5.01	5.01	µg/L
07440-28-0	Thallium	34	2	0.1	0.18	0.26	mg/L
07440-32-6	Titanium	25	1	0.06	0.06	0.06	mg/L
00108-88-3	Toluene	38	15	2.3	833	3190	µg/L
	Total Dissolved Solids	193	193	1530	63800	337000	mg/L
07440-62-2	Vanadium	24	1	40.4	40.4	40.4	mg/L
	Total Kjeldahl Nitrogen	25	25	37.5	122	585	mg/L
	Total Organic Carbon <sup>31</sup>	28	23	69.2	449	1080	mg/L
	Total Suspended Solids	43	43	16	129	2080	mg/L
	Xylenes	38	15	15.3	444	2670	µg/L
07440-66-6	Zinc	43	18	0.011	0.036	8570	mg/L
	Zinc, Dissolved	22	1	0.07	0.07	0.07	mg/L
	Fluid Density	145	145	8.39004	8.7	9.2	lb/gal
	Hardness by Calculation	170	170	203	11354	98000	mg CaCO <sub>3</sub> /L
	Salt %	145	145	0.9	5.8	13.9	%
	Specific Conductivity	15	15	1030	110000	165000	µmhos/cm
	Specific Gravity	150	154	0	1.04	1.201	
	Temperature	31	31	0	15.3	32	°C
	Temperature	145	145	24.9	68	76.1	°F

<sup>30</sup> Regulated under foaming agents.

<sup>31</sup> Regulated via BOD, COD and the different classes/compounds of organic carbon.

**Table 4-7 - Typical concentrations of parameters that are not regulated, based on limited flowback analyses from PA and WV**

<b>Parameter Name</b>	<b>Total Number of Samples</b>	<b>Detects</b>	<b>Min</b>	<b>Median</b>	<b>Max</b>	<b>Units</b>
Barium Strontium P.S.	145	145	17	1320	6400	mg/L
Carbon Dioxide	5	5	193	232	294	mg/L
Zirconium	19	1	0.054	0.054	0.054	mg/L



## **5 ON-SITE FLOWBACK FLUIDS TREATMENT OR RECYCLING TECHNOLOGIES**

### **5.1 Introduction**

New well completion and hydraulic fracturing methods are enabling the recovery of valuable onshore natural gas reserves. These new methods also require large volumes of water for the fracturing process and then produce flowback fluid with residual additives and high concentrations of a few parameters, particularly TDS, and low concentrations of several parameters.

Reasonably good quality water is typically needed to harness the full benefit of fracturing fluid additives. Freshwater is therefore an obvious choice. But use of freshwater in hydraulic fracturing operations imposes an additional constraint on the resource.

Flowback fluid disposal is also difficult. Variable percentages of fracturing fluids return to the surface as flowback. Presently, dilution and re-use at subsequent wells, trucking to approved publicly-owned treatment works (POTW) or out-of-state industrial treatment plants, or underground injection wells<sup>32</sup> are the disposal options utilized. However, treating flowback fluid at POTWs can cause potential excursion of POTW permit limits; also, trucking the water is costly. Underground injection removes the water from the natural water cycle.

On-site treatment (with off-site disposal of the contaminants removed) or recycling is seen as the more environmentally sound method for managing flowback. This section surveys on-site treatment or recycling options currently used; provides a preliminary evaluation of the extent and conditions of such use; and assesses the general applicability of these technologies at hydraulic fracturing sites in New York State.

### **5.2 Flowback Recycling**

Recycling flowback in hydraulic fracturing operations presently entails primary treatment (i.e. settling) and then blending known amounts of flowback with freshwater [3]. Recycling the flowback reduces freshwater needs. However, high concentrations of different parameters adversely affect the desired fracturing fluid properties. Concentrations of chlorides, calcium, magnesium, barium, carbonates, sulfates, solids, microbes, etc. in the flowback are too high to use as-is [1]. The demand for friction reducers increases when the chloride concentration increases [1]; the demand for scale inhibitors increases when concentrations of calcium, magnesium, barium, carbonates, or sulfates increase [1]; biocide requirements increase when the concentration of microbes increases [6]. The current recycling practice of blending flowback

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<sup>32</sup> It should be noted that while three fully permitted injection wells are operating for private oil and gas production brine disposal in New York, there are no currently operating commercial injection wells and none have been permitted for flowback injection.

with freshwater attempts to balance the additional freshwater needs with the additional additives needs.

Some form of physical and/or chemical separation (discussed later) is typically needed prior to recycling flowback.

One operator who shared analytical results after using a 50-50 blend of recycled flowback and freshwater assessed the blended water's corrosivity and scaling potential. Field experience suggests performing compatibility mixing studies prior to the actual blending flowback and freshwater in the field [20]. In addition, experts in the field suggest that flowback fluid and freshwater be evaluated multiple times during the year to assess potential seasonal variations and their impact on bacterial activity and water quality. Use of friction reducers, scale inhibitors, biocides, etc. would need to be modulated based on the composition and characteristics of the blend [20].

### **5.3 On-site Treatment**

Regardless of the treatment objective, whether for reuse or direct discharge, the three basic issues that need consideration when developing water treatment technologies are:

1. Influent [i.e. flowback] parameters and their concentrations
2. Parameters and their concentrations allowable in the effluent [i.e. the reuse or discharge water]
3. Disposal of residuals

#### **5.3.1 Influent parameters and their concentrations**

Flowback consists of several parameters. Table 4-6 and Table 4-7 provide typical concentrations of parameters in flowback. The median value would likely be the appropriate indicator of typical concentration. There is no single on-site treatment technique or on-site treatment unit, to date, that could treat all parameters in flowback. Therefore, a series of on-site treatment technologies is needed to produce a usable treated flowback stream. Stringing together several treatment units is costly. However, treating the flowback on-site would reduce freshwater needs, reduce flowback disposal costs, and depending on the final quality of the treated flowback, reduce the cost and need for additives.

#### **5.3.2 Parameters and their concentrations allowable in the effluent**

All experts and operators agree that freshwater meets the water quality needs for fracturing fluids; they also agree that somewhat lower quality water would be usable for fracturing operations. But there is no consensus on the minimum allowable water quality for a fracturing operation: different experts suggest different limits for TDS, chloride, calcium, etc. Table 5-1 is a

listing of allowable water quality requirements for fracturing fluids based on input from one expert panel [1].

**Table 5-1 – Allowable water quality requirements for fracturing fluids, based on input from one expert panel on Barnett Shale**

Constituent	Concentration
Chlorides	3,000 - 90,000 mg/L
Calcium	350 - 1,000 mg/L
Suspended Solids	< 50 mg/L
Entrained oil and soluble organics	< 25 mg/L
Bacteria	< 100 cells/100 ml
Barium	Low levels

Flowback characteristics based on limited data from PA and WV are provided in Table 4-6 and Table 4-7.

### 5.3.3 Disposal of residuals

Presently there is limited on-site treatment of flowback in the Barnett Shale due to economic infeasibility. However, based on feedback from a few operators, when on-site treatment is provided, the residuals (or concentrates) are injected into deep and stable strata (UIC wells). The regulatory framework for disposal of these residuals is complex and is further discussed later in this chapter.

### 5.3.4 Factors affecting on-site treatment

Several factors would influence the decision to utilize on-site treatment and the selection of specific treatment options. These include:

#### Operational

- Flowback fluid characteristics, including scaling and fouling tendencies
- On-site space availability
- Processing capacity needed
- Solids concentration in flowback fluid, and solids reduction required
- Concentrations of hydrocarbons in flowback fluid, and targeted reduction in hydrocarbon<sup>33</sup>
- Species and levels of radioactivity in flowback

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<sup>33</sup> Liquid hydrocarbons have not been detected in all Marcellus Shale gas analyses.

- Access to freshwater sources
- Targeted recovery rate
- Impact of treated water on efficacy of additives
- Availability of residuals disposal options

#### Cost

- Capital costs associated with treatment systems
- Transportation costs associated with freshwater
- Transportation costs associated with disposal of residuals
- Increase or decrease in fluid additives from using treated flowback fluid
- Energy costs required to run treatment systems
- Flowback storage costs

#### Environmental

- On-site topography
- Density of neighboring population
- Proximity to freshwater sources
- Other demands on freshwater in the vicinity
- Regulatory environment

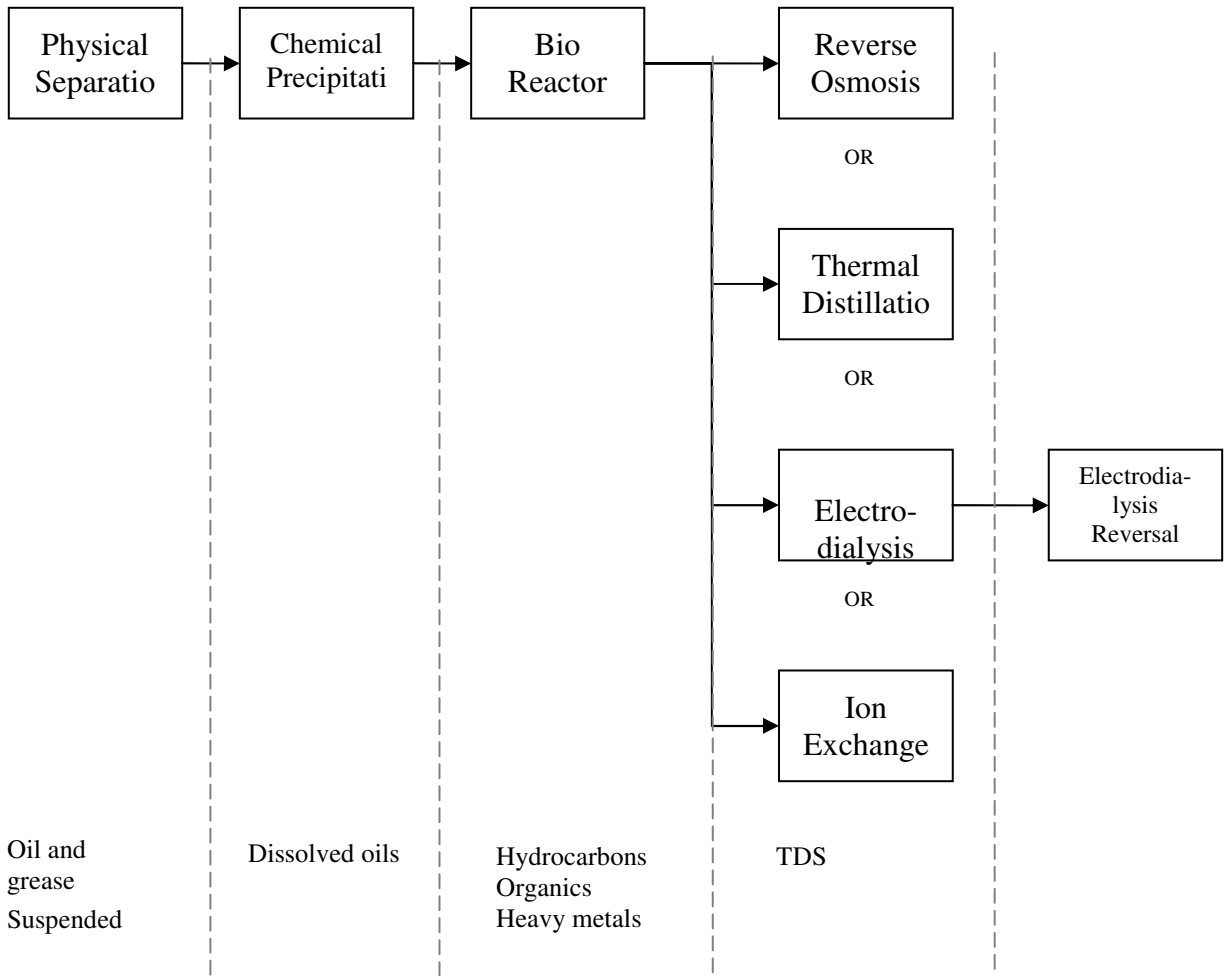
### **5.4 On-site Treatment Technologies**

One of the several on-site treatment technology configurations is illustrated in Figure 5-1<sup>34</sup>. The parameters treated are listed at the bottom of the figure. The next few sections present several on-site treatment technologies that have been used to some extent in the Barnett Shale or Powder River Basin gas extraction operations. In addition, technology providers have begun working with gas producers within the Marcellus Shale. A table summarizing many of these vendors' products is provided in Table 5-6.

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<sup>34</sup> All treatment steps illustrated in Figure 5-1 may not be necessary for flowback from each well. The particular characteristics of flowback would determine the specific steps.

**Figure 5-1 - One configuration of potential on-site treatment technologies**



Some form of physical and/or chemical separation will be required as a part of on-site treatment. Physical and chemical separation technologies typically focus on the removal of oil and grease and suspended matter from flowback.

### 5.4.1 Physical Separation

Filters, hydrocyclones and centrifuges are some of the technologies used to physically separate solids in wastewater. However, none of the flowback treatment vendors appear to utilize hydrocyclones or centrifuges in their treatment systems.

The efficiency of filtration technologies is controlled by the size and quantity of constituents within the flowback fluid as well as the pore size and total contact area of the membrane. To increase filtration efficiency, one vendor provides a vibrating filtration unit (several different pore sizes are available) for approximately \$300,000; this unit can filter 25,000 gallons per day.

Microfiltration has been shown to be effective in lab-scale research, nanofiltration has been used to treat produced water from off-shore oil rigs, and modular filtration units have been used in the Barnett Shale and Powder River Basin [21, 22, 23, 24].

### **5.4.2 Chemical Separation and Precipitation**

Chemical separation utilizes coagulants and flocculants to break emulsions (dissolved oil) and to remove suspended particles. Precipitation is accomplished by manipulating flowback chemistry such that constituents within the flowback (in particular, metals) will precipitate out of solution. This can also be performed sequentially, so that several chemicals will precipitate, resulting in cleaner flowback.

Separation and precipitation are used as pre-treatment steps within multi-step on-site treatment processes. Chemical separation units have been used in the Barnett Shale and Powder River Basin, and some vendors have proprietary designs for sequential precipitation of metals for potential use in the Marcellus Shale [25, 26, 27].

If flowback is to be treated solely for blending and re-use as fracturing fluid, chemical precipitation may be one of the only steps needed. By precipitation of scale-forming metals (e.g. barium, strontium, calcium, magnesium), minimal excess treatment may be required. Prices for chemical precipitation systems are dependent upon the cost of the treatment chemicals; one vendor quoted a 15 gallon per minute (gpm) system for \$450,000 or a 500 gpm system for approximately \$1 million, with costs ranging from \$0.50 to \$3 per barrel.

### **5.4.3 Membranes / Reverse Osmosis**

Membranes are an advanced form of filtration, and may be used to treat TDS in flowback. The technology allows water, the permeate, to pass through the membrane but the membrane blocks passage of suspended or dissolved particles larger than the membrane pore size. This method may be able to treat TDS concentrations up to approximately 45,000 mg/L, and produce an effluent with TDS concentrations between 200 and 500 mg/L. This technology generates a residual, the concentrate, which would need proper disposal. The flowback recovery rate for most membrane technologies is typically between 50 and 75 percent. It is important to note that membrane performance is typically impacted by scaling and/or microbiological fouling; therefore, flowback requires extensive pretreatment before it can be sent through a membrane.

Reverse osmosis (RO) is a membrane technology that uses osmotic pressure on the membrane to provide passage of high quality water, producing a concentrated brine effluent that will require further treatment and disposal. RO is frequently used in various desalination projects, in both modular and permanent configurations.

RO is a well-proven technology, though it is less efficient under high TDS concentrations. High TDS concentrations, such as in Marcellus flowback (Table 4-6), will likely result in large quantities of concentrated brine (or reject) that will require further treatment or disposal. When designing treatment processes, several vendors use RO as a primary treatment (with appropriate

pre-treatment prior to RO); and then use a secondary treatment method for the concentrated brine. The secondary treatment can be completed on-site, or the concentrated brine can be trucked to a centralized brine treatment facility.

Modular membrane technology units have been used in many different regions for many different projects, including the Barnett Shale. Some firms have developed modular RO treatment units, which could potentially be used in the Marcellus [28, 29, 30, 31, 32].

#### 5.4.4 Ion Exchange

Ion exchange units utilize different resins to preferentially remove certain ions. When treating flowback, the resin would be selected to preferentially remove sodium ions. The required resin volume and size of the ion exchange vessel would depend on the salt concentration and flowback volume treated.

The Higgins Loop is one version of ion exchange that has been successfully used in Midwest coal bed methane applications. The Higgins Loop uses a continuous countercurrent of flowback fluid and ion exchange resin. High sodium flowback fluid can be fed into the absorption chamber to exchange for hydrogen ions. The strong acid cation resin is advanced to the absorption chamber through a unique resin pulsing system [33].

Modular ion exchange units have been used in the Barnett Shale.

#### 5.4.5 Electrodialysis

These treatment units are configured with alternating stacks of cation and anion membranes that allow passage of flowback fluid. The electric current applied to the stacks forces anions and cations to migrate in different directions [32].

Electrodialysis Reversal (EDR) is similar to electrodialysis, but its electric current polarity may be reversed as needed. This current reversal acts as a backwash cycle for the stacks, which reduces scaling on membranes. EDR offers lower electricity usage than standard RO systems and can potentially reduce salt concentrations in the treated water to less than 200 mg/L.

Modular electrodialysis units have been used in the Barnett Shale and Powder River Basin.

**Table 5-2 - Treatment capabilities of EDR and RO Systems**

Criteria	EDR	RO
Acceptable influent TDS (mg/L)	400-3,000	100-15,000
Salt removal capacity	50-95%	90-99%
Water recovery rate	85-94%	50-75%
Allowable Influent Turbidity	Silt Density Index (SDI) < 12	SDI < 5
Operating Pressure	<50 psi	> 100 psi
Power Consumption	Lower for <2,500 mg/L TDS	Lower for >2,500 mg/L TDS

Criteria	EDR	RO
Typical Membrane Life	7-10 years	3-5 years

#### 5.4.6 Thermal Distillation/Evaporation

Thermal distillation utilizes evaporation to produce clean, distilled water from the flowback fluid. The various evaporative schemes that can be used within this process are generally insensitive to scaling, and are therefore more effective at higher TDS concentrations (>150,000 mg/L) than other treatment technologies.

Traditionally energy and space intensive, recent industry advancements have produced modular distillation/evaporation units that are less cost-prohibitive than older models. Some systems have been designed with the option to utilize natural gas that may be available from the well pad<sup>35</sup>, while others use recycled waste heat (primarily from gas compressors at the well pad) as the sole heat source. In addition to new sources of thermal energy for distillation systems, some vendors have designed systems that require significantly less energy than traditional distillation processes. While this makes thermal distillation a more feasible approach to flowback water treatment, these lower energy systems are most effective on highly concentrated wastewaters, thus minimizing the amount of water needed to be evaporated. Due to these limitations, some vendors suggest that thermal distillation/evaporation be used as a secondary treatment; further concentrating the wastewater concentrate from a filtration or reverse osmosis treatment system.

Modular thermal distillation units have been used in the Barnett Shale, and have begun to be used in the Marcellus Shale in Pennsylvania. In addition to the units that are already in use, several vendors have designs ready for testing, potentially further decreasing costs in the near-future [23, 24, 30, 34, 35, 36, 37, 38].

Due to the high TDS concentrations found in Marcellus flowback samples, mobile evaporation treatment systems appear to be the most feasible system for treatment of flowback water. Many vendors who supply evaporation units offer rentals that may be paid for on a volumetric basis. Rate quotes from vendors are provided in Table 5-6; the rates are within the general range of \$3 to \$4.50 per barrel of flowback.

#### 5.4.7 Crystallization/Zero Liquid Discharge

Zero liquid discharge (ZLD) follows the same principles as physical and chemical separation (precipitation, centrifuges, etc.) and evaporation, however a ZLD process ensures that all liquid effluent is of reusable or dischargeable quality. Additionally, any concentrate from the treatment process will be crystallized and will either be used in some capacity on site, will be offered for

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<sup>35</sup> During initial exploration and production phases, natural gas would likely not be readily available at the well pad.



sale as a secondary product if radiological parameters are below an acceptable threshold, or will be treated in such a way that it will meet regulations for disposal within a landfill.

ZLD treatment is a relatively rare, expensive treatment process, and while some vendors suggest that the unit can be setup on the well pad, a more cost-effective use of ZLD treatment will be at a centralized treatment plant located near users of the systems' byproducts. In addition to the crystallized salts produced by ZLD, treated effluent water and/or steam will also be a product that can be used by a third party in some industrial or agricultural setting.

ZLD treatment systems are in use in a variety of industries, but none have been implemented in a natural gas production setting yet. Some technology vendors have advertized ZLD as a treatment option in the Marcellus, but the economical feasibility of such a system has not yet been demonstrated [30, 35, 37, 38].

#### 5.4.8 Ozone/Ultrasonic/Ultraviolet

These technologies are designed to oxidize and separate most hydrocarbons and heavy metals, and oxidize biological films and bacteria from flowback fluid. The microscopic air bubbles in supersaturated ozonated water and/or ultrasonic transducers cause oils and suspended solids to float.

Multiple vendors include ozone treatment technologies as one step in their flowback treatment process, including treatment for blending and re-use of water in drilling new wells. Systems utilizing ozone technology have been successfully used and analyzed in the Barnett Shale [31, 39].

#### 5.4.9 Comparison of potential on-site treatment technologies

A comparison of performance characteristics associated with on-site treatment technologies is provided in Table 5-3.

**Table 5-3 - Summary of Characteristics of On-site Flowback Fluid Treatment Technologies**

Characteristic	Filtration	Ion Exchange	Reverse Osmosis	EDR	Thermal Distillation	Ozone / Ultrasonic / Ultraviolet
Energy Cost	Low	Low	Moderate	High	High	Low
Energy Usage vs. TDS	N/A	Low	Increase	High Increase	Independent	Increase
Applicable to	All Water types	All Water types	Moderate TDS	High TDS	High TDS	All Water types
Plant / Unit size	Small / Modular	Small / Modular	Modular	Modular	Large	Small / Modular

<b>Characteristic</b>	<b>Filtration</b>	<b>Ion Exchange</b>	<b>Reverse Osmosis</b>	<b>EDR</b>	<b>Thermal Distillation</b>	<b>Ozone / Ultrasonic / Ultraviolet</b>
Microbiological Fouling	Possible	Possible	Possible	Low	N/A	Possible
Complexity of Technology	Low	Low	Moderate / High Maintenance	Regular Maintenance	Complex	Low
Scaling Potential	Low	Low	High	Low	Low	Low
Theoretical TDS Feed Limit (mg/L)	N/A	N/A	32,000	40,000	100,000+	Depends on turbidity
Pretreatment Requirement	N/A	Filtration	Extensive	Filtration	Minimal	Filtration
Final Water TDS	No impact	200-500 ppm	200-500 ppm	200-1000 ppm	< 10 mg/L	Variable
Recovery Rate (Feed TDS >20,000 mg/L)	N/A	N/A	30-50%	60-80%	75-85%	Variable

## 5.5 On-site containment of flowback

Specific regulations applicable to containment of waste streams are typically governed by the type (classification) of waste. The following sections discuss the available containment vessels, and the regulations that could potentially apply to flowback.

Due to the large volumes of water required for hydraulic fracturing operations and the limited quantities of water that can be withdrawn and transported in a single day, some form of on-site containment is needed. The two predominant methods of achieving on-site containment are the construction of artificial impoundments and the use of portable water tanks, commonly called frac tanks. Typically, operators utilize a combination of impoundments and frac tanks.

### 5.5.1 Frac tanks

Frac tanks are available from many different vendors and, for the most part, follow similar patterns of design. Whether a producer chooses to purchase or to rent frac tanks, there are essentially three designs from which to choose.

The most prevalent design is a 21,000-gallon, V-bottom, rectangular tank with a single axle. These tanks are designed to be pulled by any semi-truck with a fifth-wheel hitch. The V-shaped bottom of the tank allows for easy cleaning of the interior of the tank (which must be done to prolong tank life).

Another popular design is very similar to the previous one, however instead of a V-bottom, these tanks have a cylindrical bottom. Functionally, there is not much difference between these two tank designs.

The third frac tank design is a skid-mounted cylindrical tank. The main difference between these tanks and the wheeled, rectangular tanks previously described is that the cylindrical tanks must be loaded onto a flat-bed trailer for transport. While tank transport may be more challenging for these tanks, they are available in volumes larger than the 21,000-gallon rectangular tanks.

Most frac tanks are designed to have at least one man-way, which allows access to the interior of the tank for cleaning and maintenance. Additional features that are commonly installed include: interior weirs to allow for solids settling, interior epoxy coating to minimize corrosion, volume gauges, and various adjustable piping and drainage configurations. Many manufacturers also supply geomembrane containment berms that are designed to sit under the frac tanks which will capture any spills or stray fluids that escape the tanks. Some manufacturers also offer double-walled tanks for an extra level of protection; these tanks typically offer less capacity than the 21,000, single-walled tanks.

Each frac tank is capable of holding only a small portion of the frac fluid or flowback at any given time. To account for this, operators use hoses and connections to connect (“gang”) several frac tanks together. If an operator were using the standard 21,000-gallon frac tank, 48 completely filled tanks would be required to hold a million gallons of fluid on-site. This ganged configuration results in large and variable capacity of the water storage system, a feature not available if using only an on-site impoundment, however this could prove to be a costly and space-consuming approach to on-site fluid containment.

### **5.5.2 On-site impoundments (storage pits)**

In coordination with frac tanks or alone, some form of on-site impoundment is typically needed for hydraulic fracturing operations. In addition to holding water for fracturing and storing flowback, impoundments are commonly used by drillers to hold water and drilling mud, as well as by producers to hold produced water and other wastewaters and brines created at the well-site. The use of these impoundments, as well as their design, is typically controlled by various state regulations. While many states have such regulations, this section of the report will compare regulations governing impoundments from two states with current natural gas operations (Texas and Pennsylvania) to the comparable, existing New York state regulations.

Many aspects of Texas’ and Pennsylvania’s impoundment regulations are complementary; however they are implemented in slightly different ways. There are three broad differences between the two states’ regulations on impoundments. These are in:

1. The approval process;
2. Use of synthetic liners; and
3. Need for leak detection.

Texas regulation governing the use of storage pits states that the Texas Railroad Commission must approve of the pit design before any oil or gas operator is permitted to use an on-site impoundment [40]. The Commission has published a guidance manual specifying design criteria which are deemed appropriate [41]. Pennsylvania, on the other hand, incorporated the design criteria into the actual regulations [42].

The most significant difference between these two states' containment regulations is in the use of synthetic liners. Pennsylvania requires the use of such a liner for all oil and gas-related containment ponds; however, Texas allows use of compacted soil without a synthetic liner for certain types of containment ponds. Large portions of Texas are underlain by clay soils that, when compacted, are expected to meet the state's permeability requirement. Although not applicable for many pits, this potentially gives Texas gas operators, upon regulatory approval, the ability to utilize unlined, compacted soil containment ponds – a design option not available in Pennsylvania [41].

The other significant difference between these two states' regulations is the requirement for leak detection systems for brine containment pits. Texas regulation requires leak detection systems for brine containment pits that use a synthetic liner. Other pit types may not be required to have a leak detection system, unless determined to be in a hydrologically sensitive area (e.g., regions where the groundwater is close to the surface). Pennsylvania, on the other hand, does not require a leak detection system. If a liner's integrity is found to be compromised, alternative storage or disposal of the waste must be completed, however there is no regulation requiring an early-detection system for leaks from on-site containment ponds in Pennsylvania.

**Table 5-4 - Design specifications for containment ponds as required by state regulations**

<b>Design Requirement</b>	<b>Texas</b>	<b>Pennsylvania</b>
Relevant Code	Title 16: Economic Regulation §3.8: Oil and Gas Division – Water Protection  Specifications from: Surface Waste Management Manual Chapter IV: Pits	Title 25: Environmental Protection §78.56: Oil and Gas Wells – Environmental Protection Performance Standards
Required Freeboard	Requires that freeboard be “consistent with the volume of wastewater to be retained”	Requires 2 feet of freeboard (unless connected to overflow tanks)
Liner	No liner required if compacted soil's permeability is $10^{-7}$ cm/sec or less, and is at least 2 feet thick	Synthetic flexible liner required
Maximum liner permeability	Not explicitly listed, but no more than $10^{-7}$ cm/sec	$10^{-7}$ cm/sec
Seam joining	Factory seams when possible – seams oriented up and down a slope, not across – installed by qualified personnel – minimize number of seams	Must be leak-proof, installed per manufacturer's instructions

<b>Design Requirement</b>	<b>Texas</b>	<b>Pennsylvania</b>
Long-term stability of liner	Chemical compatibility with waste; mechanical stability during: transport, installation, settlement of base soils; resistant to UV damage	Not to be physically or chemically damaged by: waste, transportation, handling, installation, or use
Liner subbase	Compacted soil – remove rocks and jagged irregularities and debris	Smooth, uniform, and free of materials that may cause liner to fail – 6 inches of soil or gravel must be between liner and rock layers
Height above groundwater	Varies - if groundwater is close to surface, above ground pit may be required	20 inches above seasonal high water table
Leak protection	Leak detection system required for synthetic liners – required for any pit in a sensitive area	Managed to preserve liner integrity – if not able, materials must be removed and disposed
Filling of pit	Individual permits will have requirements for backfilling pits	Unless holding material for disposal, pit must be removed or filled within 9 months after well-drilling is completed (90 days if used for well servicing, plugging, or recompleting)
Alternative designs	Flexible regulations provide for different design approaches, including other liner systems	Alternate designs - PADEP approval required prior to construction

New York State code allows for oil/gas field brine storage, for a limited time, in watertight tanks, containers or earthen pits, if underlain by clay or hardpan, and constructed and maintained so as to prevent escape of brine or salt water[43]. See Section 4.7.2 for additional information. The GEIS further requires use of a plastic liner for all pits and specifies pit design and construction procedures [18].

The regulated design criteria for solid waste disposal pits in New York are similar to regulations in place for water/flowback storage impoundments in other oil and gas producing states. These regulations require double-lined systems, with a leak detection system, as well as several groundwater monitoring wells [44].

In addition to regulations in place in other states, more stringent state regulation of on-site impoundments for oil and gas wastes (including flowback) is recommended by the USEPA. As discussed in the following section, adequate state regulation of impoundment design was one of the driving reasons the USEPA exempting oil and gas wastes from certain federal waste management regulations. Where adequate state regulations do not exist, the USEPA recommends that potential deficiencies in the state regulations be addressed appropriately.

## 5.6 Exemption of oil and gas waste from federal regulations

On-site treatment and containment of drilling mud and flowback fluids requires compliance with federal and state regulations. However, this industry is presently exempt from some of the more stringent federal regulations. The Resource Conservation Recovery Act (RCRA) governs how waste materials are handled and disposed of, including a subcategory of solid wastes that are defined as hazardous. Depending on the specific constituents in flowback from a particular site/location, as defined by the RCRA, flowback fluid may be considered a solid waste [45]; however, regardless of the fluid's Toxicity Characteristics, because of its exemption from RCRA, flowback will be exempt from federal classification as a hazardous waste [46, 47].

The USEPA reviewed existing regulations prior to preparing its 1988 regulatory determination resulting in the exemption of oil and gas exploration and production wastes from federal hazardous waste regulations [48]. That review resulted in the following conclusions:

- Many samples of oil and gas exploration and production wastes exhibited toxic characteristics, although these characteristics alone do not indicate the actual threat to human or environmental health. Location and management practices, among other factors, help to reduce risks from these wastes.
- Categorizing these wastes as hazardous under RCRA would have a large (multi-billion dollar) economic impact upon the oil and gas industry, with some of the impact being passed on to consumers, ultimately resulting in as much as an estimated 12% decrease in production.
- Existing state and federal regulations should provide effective regulation of oil and gas wastes, without requiring the stringent RCRA hazardous waste regulation.
- Certain state regulations, including the design and maintenance criteria for waste containment ponds, may not be adequate.

Table 4-6 is a summary of flowback constituents-related data provided by industry via NYSDEC. Similar to the USEPA study, concentrations of most constituents in Table 4-6 are lower than required for classification as hazardous due to toxicity. Median concentrations of barium, benzene and mercury come close to (or exceed) the regulatory toxicity level. It is important to note that, per 40 CFR 261.24, toxic concentrations need to be determined using specifically prescribed analytical methods; these methods were not used for analyses reported in Table 4-6.

Barium was detected in nearly all flowback samples that analyzed for barium. This is expected: barium is a component of most drilling muds and would therefore be present in flowback. The maximum concentration of barium for the Toxicity Characteristic, as provided in 40 CFR 261.24, is 100 mg/L. The median concentration of barium in Table 4-6 is approximately 1500 mg/L.

Similarly, benzene was detected in several flowback samples that analyzed for it. The maximum concentration of benzene for the Toxicity Characteristic, as provided in 40 CFR 261.24, is 0.5

mg/L. The median concentration of benzene found in samples that analyzed for it was approximately 0.5 mg/L.

Similarly, the mercury Toxicity Characteristic concentration is 0.2 mg/L. The median mercury concentration in Table 4-6 is nearly 0.3 mg/L.

While it is acknowledged that oil and gas exploration and production wastes may indeed have toxic characteristics, the EPA concluded that the economic burden imparted on operators if these wastes were regulated under RCRA hazardous waste rules was not justified, given other federal waste regulations and additional state regulations already in place.

In addition, the USEPA found that state and federal regulations already in place are sufficient for protecting the environment and the public from the hazardous characteristics of these wastes. The USEPA argued that the systems in place to protect surface water (National Pollutant Discharge Elimination System – NPDES; SPDES in New York) and groundwater (Underground Injection Control - UIC) from pollution would regulate the ultimate fate of these wastes.

## 5.7 Naturally Occurring Radioactive Materials and Water Treatment

All environmental media contain Naturally Occurring Radioactive Materials (NORM) and is radioactive to some degree. NORM is often exposed during drilling, flowback and production operations and may be of particular concern in the Marcellus Shale. Flowback can carry NORM with it when it returns to the well pad surface. Radium-226 has a 1,600 year half-life, is commonly occurring, and undergoes alpha decay. Radium-228 has a half-life of 5.76 years, and undergoes beta decay [49].

Alpha and beta radiation, indicators of radioactive decay, were each detected in all flowback samples that tested for them. Additionally, some samples were tested for radium-226 and radium-228. These results were summarized in Table 4-6, and repeated below in Table 5-5.

The use of gross alpha and beta analyses as indicators of the concentration of radium isotopes may be limited due to the variability in the correlation between gross analytical results and concentrations of Ra-226 ad 228.

The MSC Study Report does not evaluate NORM.

**Table 5-5 – Radiological data in limited flowback analyticals from PA and WV**

Parameter	Total Number of Samples	Number of Detects	Minimum	Median	Maximum	Units
Radium	6	3	7.7	9.7	24	pCi/L
Radium 226	3	3	2.58	4.67	33	pCi/L
Radium 228	3	3	1.15	4.66	18.41	pCi/L
Alpha radiation	15	15	0	166	18950	pCi/L
Beta radiation	15	15	0	62	7445	pCi/L

### **5.7.1 Federal and state regulations regarding NORM**

The reported levels of NORM in Marcellus Shale flowback samples are relatively low. Limited data from PA and WV has indicated higher NORM concentrations in later flowback water than in the initial flowback water. Based on limited data, it appears that NORM concentrations in production brine are higher than in flowback water.

Treatment of flowback water or production brine could result in the presence of “processed and concentrated NORM,” also known as “technologically-enhanced” NORM (TENORM) in the concentrated brine, solids, or sludge, which could potentially be subject to regulation under 6 NYCRR Part 380. At the federal level, jurisdictional agencies may include the USEPA, the Nuclear Regulatory Commission (NRC), Occupational Safety and Health Administration (OSHA), and Pipeline and Hazardous Materials Safety Administration (PHMSA). In the absence of any delegated state authority, these agencies would have regulatory jurisdiction at various points throughout the waste treatment, transportation and disposal processes [50].

Various individual states have introduced regulations related to NORM and TENORM, including regulatory frameworks for NORM disposal, as described below. In New York, many NORM-related regulatory responsibilities lie with the NYS Departments of Environmental Conservation (NYSDEC) and Health (NYSDOH). The NYSDEC has radiological regulatory authority as well as waste regulatory authority, and NYSDOH has regulatory authority over worker and public health protection from radiation along with the authority and responsibility to issue licenses to operators where radioactivity levels meet specified thresholds.

### **5.7.2 Disposal of TENORM produced by natural gas drilling**

Efficient wastewater treatment processes typically achieve a high water recovery rate by concentrating the solids/sludges, etc. While there are several treatment technologies or methods (discussed in Section 5.4) that could potentially treat flowback for one or more constituents, at present, there is no practical and cost-effective method to selectively remove NORM or processed and concentrated NORM. Therefore the impact of concentrating waste streams that could potentially contain NORM must be considered by gas developers and treatment plant operators.

Some states have implemented regulatory frameworks for disposal of oil-and-gas-associated waste streams that could contain NORM. The most frequently mentioned methods of disposal are:

- On-site injection into oil/gas well once production has ceased.
- On-site spreading of waste on land (incorporation into topsoil).
- Off-site injection into permitted disposal wells.
- Road application of brine for ice melting purposes [56].
- Disposal at permitted RCRA C facilities.



- Disposal at permitted low-level radioactive waste repositories (this is a last resort disposal method).
- Off-site brine treatment facilities (permitted to treat produced waters and brines – potentially limited influent NORM levels).

Note that not all these methods are allowed or implemented in all states with oil and gas production. In particular, New York’s Part 380 regulations do not provide for a land spreading option and the process required under 6 NYCRR Part 364 for a Beneficial Use Determination to allow road application would consider radioactivity levels and result in a denial if a public health concern is determined to exist.

In addition to the flowback water and/or treatment concentrates containing NORM or TENORM, any equipment used onsite has the potential to become contaminated with built-up radioactive material. To address this issue, some states with significant oil and gas production have also implemented regulations governing the decontamination and re-use and/or disposal of such equipment.

### **5.7.3 Pre-treatment potential for radium**

At present, there does not appear to be a commercially used<sup>36</sup> treatment method that selectively treats/removes radium from flowback or production brine. Chemical precipitation, for example, is based on the chemical’s solubility constant/product. The solubility of radium and its compounds is similar to the solubility of several other metals and their compounds. Therefore isolating it via precipitation, when treating large volumes of waste streams, would be challenging.

Treatment techniques, such as chemical precipitation, ion-exchange or activated carbon that remove radium also remove other metals. The treatment capacity (chemical usage, size of ion-exchange unit, size of carbon beds, etc.) therefore needs to be sufficiently large to accommodate all similar metals in flowback and production brine. Any flowback treatment system would have sludge and rejects handling needs; the presence of NORM or processed and concentrated NORM would elevate the standard of care needed for handling sludge and rejects [57]. Several of the vendors of treatment technologies listed in Table 5-6 suggest removing radium at an earlier phase in the treatment process to avoid potential contamination of subsequent treatment units.

Because of the potential challenges with handling waste streams that may contain processed and concentrated NORM, treating flowback with appreciable amounts of NORM would be difficult.

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<sup>36</sup> Here ‘Commercial Use’ encompasses wastewater treatment beyond flowback, but takes into consideration the potential large volumes that would need handling.

## 5.8 Summary

While costly, on-site treatment of flowback water may offer many advantages to Marcellus gas operators. Treatment and re-use of flowback will reduce the quantity of fresh water required for fracturing operations, which will in turn reduce withdrawal and trucking costs. On-site treatment may also potentially reduce disposal cost of flowback fluids, by decreasing volumes that must be trucked to a centralized treatment facility or disposal site.

On-site treatment technology is not necessarily widely available, although an increasing number of producers are beginning to use such systems within the Marcellus Shale in various capacities. On-site treatment technologies would likely evolve more rapidly when industry need and regulatory environment call for it.

Several challenges would need to be overcome to successfully implement on-site treatment and/or re-use of flowback water. The uncertainties associated with minimum water quality that may be utilized in fracturing operations, the large fluctuations in flowback quality, and the differences in quality of flowback from different shale formations are all potential issues that must be addressed.

In addition to the above uncertainties, storage, handling, and ultimate disposal of flowback concentrates could become further complicated by its potentially hazardous or radioactive properties.

While presently exempt from federal hazardous waste regulations, flowback's potential hazardous characteristics should be considered when designing on-site containment systems.

Several new flowback treatment systems have been proposed and tested in the last few years. Treatment capability will likely continue to improve and treatment costs will likely decline as the oil and gas industry begins to utilize treatment technologies more extensively.

**Table 5-6 - Select characteristics of various treatment technologies currently offered or under design<sup>37</sup>**

Vendor	Processes used	Flowrate/unit	Allowable Influent TDS	% Recovered as Effluent	Effluent quality	Footprint/ unit	Energy Usage	Approximate Price	Description of concentrate	Concentrate disposal method	Operational Status
A & B	Thermal Distillation/ Evaporation	720,000 gpd	10,000 mg/L	>95%	<5 mg/L TDS	Onsite/ modular in addition to a centralized plant	High	---	Rock salts or concentrated brine	Rock salt can be sold - concentrated brine must be treated	Portable unit is designed - centralized treatment facility is being designed
	Crystallization		150,000 mg/L	50%							
B	Brine concentration	---	---	>95%	<10 mg/L TDS	Onsite/ modular units or centralized treatment plant	Moderate to high	\$50M-\$100M for centralized treatment plant	Concentrated brine or crystallized solids	Brine must be treated or - solids can be re-used, sold, or disposed	Vendor has extensive experience with centralized treatment plants
	Evaporation	---	---	---	---						
	Crystallization	---	---	---	---						
	Reverse Osmosis	662,400 gpd	45,000 mg/L	35-45%	---						
C & D	Chemical Precipitation	100,000 gpd	custom	custom	---	Onsite/ modular	Low	---	---	---	Designed, not yet implemented
	Oxidation										
E	Oxidation	---	40,000 mg/L chloride	---	on-site reuse	Onsite/ modular - contained in frac tanks	Moderate	Contracted price per barrel	---	---	Field tested
	Reverse Osmosis										
F & G	Filtration	126,000 gpd/unit	---	90-95%	distilled water (<200 mg/L TDS)	Onsite/ portable	High	\$3-\$4 per barrel	Concentrated brine	Injection well or further treatment	Used by many industries - starting to be used in field for flowback - contains process to separate VOCs for use
	Thermal Distillation/ Evaporation								Onsite use or sale		
	Oxidation									VOCs	
H	Nanofiltration w/ vibration	316,800 gpd	discharge or reuse	80%	injection well	4'x4'x16'H	Low to moderate	\$300,000 for a 25,000 gpd unit	5% total solids	Injection well or further treatment	In use in Marcellus and on offshore oil rigs
I	Thermal Distillation/ Evaporation	72,000 gpd	---	---	for blending and reuse	Onsite/ modular	Moderate to high	\$4 per barrel	Concentrated brine	Injection well or further treatment	Ready to be built
	Reverse Osmosis	1,008,000 gpd	---	75%		---	Moderate				
J	Thermal Distillation/ Evaporation	330 gpd/unit	150,000 mg/L (41,700 mg/L in test results)	90%	< 500 mg/L TDS (106 mg/L TDS in test results)	~ 10 ft <sup>2</sup> /unit	Moderate (low energy evap)	---	---	---	In use in western US and in PA for treating produced water - also building centralized plant
K	Reverse Osmosis	4,500 gpd/unit	45,000 mg/L	---	drinking quality	36' x 7' - modular	Moderate	---	Concentrated brine	---	Tested - for sale
L	Evaporation & Crystallization	---	---	95%	reuse/ discharge	Onsite/ modular units or centralized treatment plant	High	---	Solid cake	Approved for landfill disposal	Custom design - not implemented in Marcellus yet
M	Filtration	~20,000 gpd/unit	no limit	90%	steam	20' x 40'	Low (waste heat)	\$3-\$4 per barrel	Concentrated brine or chemical crystallization	Brine treatment plant or landfill for the crystals	In use in Marcellus in PA
	Evaporation										
	Crystallization										

<sup>37</sup> This table contains data obtained from flowback treatment system vendors. This information may change at anytime and its inclusion in this table by no means indicates a preference or an endorsement of any one technology (vendor names have been omitted). Vendors providing different types of treatment units sometimes collaborate in order to provide a complete treatment system.

Vendor	Processes used	Flowrate/unit	Allowable Influent TDS	% Recovered as Effluent	Effluent quality	Footprint/ unit	Energy Usage	Approximate Price	Description of concentrate	Concentrate disposal method	Operational Status
N	Distillation (Mobile Vapor Recompression)	105,000 gpd/unit	80,000 mg/L	60-90%	<10 mg/L TDS	50' x 50'	Moderate	\$4.50 per barrel	Concentrated brine	Centralized treatment or reuse as a kill fluid	In use in western US
	Mechanical/ chemical separation										
O	Chemical Precipitation	300,000 gpd	---	---	re-use as fracturing fluid	25,000 ft <sup>2</sup>	Low	\$0.50 - \$3 per barrel	Sludge cake	Landfill if barium is removed from sludge - otherwise, hazardous waste	Process designed - not implemented yet

## **6 POTENTIAL ENVIRONMENTALLY-FRIENDLY FRACTURING AND STIMULATION TECHNOLOGIES**

### **6.1 Introduction**

Hydraulic fracturing operations involve the use of significant quantities of additives/products, albeit in low concentrations, which potentially could have an adverse impact on the environment if not properly controlled. The recognition of potential hazards has motivated investigation into environmentally-friendly alternatives for hydraulic fracturing technologies and chemical additives.

It is important to note that use of ‘environmentally friendly’ or ‘green’ alternatives may reduce, but not entirely eliminate, adverse environmental impacts. Therefore, further research into each alternative is warranted to fully understand the potential environmental impacts and benefits of using any of the alternatives. In addition, the ‘greenness’ needs to be evaluated in a holistic manner, considering the full lifecycle impact of the technology or chemical.

### **6.2 Environmentally-Friendly Fracturing Technology Alternatives**

The following environmentally-friendly technology alternatives have been identified as being in use in the Marcellus Shale, with other fracturing/stimulation applications or under investigation for possible use in Marcellus Shale operations:

- Liquid carbon dioxide alternative – The use of a liquid carbon dioxide and proppant mixture reduces the use of other additives [51]. Carbon dioxide vaporizes leaving only the proppant in the fractures. The use of this technique in the US has been limited to demonstrations [93].
- Nitrogen-based foam alternative – Nitrogen-based foam fracturing was used in vertical shale wells in the Appalachian Basin until recently [87]. Nitrogen gas is unable to carry appreciable amounts of proppant and the nitrogen foam was found to introduce liquid components that can cause formation damage [88].
- Liquefied Petroleum Gas (LPG) – The use of LPG, consisting primarily of propane, has the advantages of carbon dioxide and nitrogen cited above; additionally, LPG is known to be a good carrier of proppant due to the higher viscosity of propane gel [83]. Further, mixing LPG with natural gas does not ‘contaminate’ natural gas; and the mixture may be separated at the gas plant and recycled [83]. LPG’s high volatility, low weight, and high recovery potential make it a good fracturing agent. This technology is in limited use in Canada, and no information is publicly available about any use in the US.
- Horizontal and directional wells – These techniques are already in widespread use in the Marcellus Shale and other shale gas formations. While these techniques require larger quantities of water and additives per well, horizontal and directional wells are

considered to be more environmentally-friendly because these types of wells provide access to a larger volume of gas/oil than a typical vertical well [93, 89].

Several unconventional drilling techniques (e.g. slimhole drilling, coiled tubing, multilateral drilling, and dual-well configuration<sup>38</sup>) have made advances in recent decades and are considered to be more environmentally-friendly [90, 91, 93, 58, 85] because of their smaller footprint. But there are no known instances of their use at shale plays similar to the Marcellus.

Locating multiple wells in a single pad, particularly multiple horizontal wells in a single pad, is a widely used technique that reduces the overall surface footprint.

### **6.3 Environmentally-Friendly Chemical Alternatives**

The most significant environmentally friendly change made to date in shale fracturing operations in the United States has been the switching from a diesel- (also called oil- or synthetic-) based fluid to water based fluid. In 2003, BJ Services Company, Halliburton Energy Services, Inc., and Schlumberger Technology Corporation and the USEPA signed a voluntary Memorandum of Agreement by which diesel fuel use in hydraulic fracturing fluids injected into underground sources of drinking water during hydraulic fracturing of coalbed methane wells was eliminated [59, 60]. Diesel contains benzene, naphthalene, toluene, ethylbenzene, xylenes, and other potentially harmful compounds. While this agreement was limited to shallow coalbed methane wells, diesel was not among the listed constituents used for hydraulic fracturing by operators or their service providers who shared data with NYSDEC, and its use as a primary component of hydraulic fracturing fluid is not within the scope of the SGEIS. While chemical additives are still involved, the fluid used in hydraulic fracturing operations is now water-based.

There are several US-based chemical suppliers who advertise ‘green’ hydraulic fracturing additives. For example, Earth-friendly GreenSlurry system from Schlumberger used in both the U.K. North Sea and the Gulf of Mexico [61]; Ecosurf EH surfactants by Dow Chemicals; or ‘Green’ Chemicals for the North Sea from BASF. USEPA has published the twelve principles of green chemistry and a sustainable chemistry hierarchy [62], listed below, yet these do not provide a common measure of environmental-friendliness to assess ‘green’ hydraulic fracturing additives.

#### USEPA’s twelve principles of green chemistry

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.

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<sup>38</sup> The dual-well configuration combines a vertical and intersecting horizontal wellbore systems to access greater extents of gas resources with a single well site. This has been applied in low-medium permeability formations.

2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.
3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. Use renewable feedstocks: Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.
10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

While these twelve principles of green chemistry and a sustainable chemistry hierarchy set general characteristics of an environmentally-friendly chemical or technique, they do not provide an objective metric for evaluating the environmentally-friendliness. Presently, environmentally-friendliness of chemicals used in hydraulic fracturing in the US has been measured only subjectively. Vendors/suppliers indicate their products are environmentally-friendly, but presently, there is no established method in the US to assess the life-cycle

impact or impact on all relevant media of these chemicals. The next few sections discuss objective metrics used elsewhere in the world.

### **6.3.1 Experience from Drilling in the North Sea**

Much of the knowledge regarding environmentally-friendly chemicals used with gas exploration is based on drilling operations in the North Sea. Strict environmental guidelines regulate the amounts and types of chemicals that may be discharged into the North Sea. Two of the initiatives are:

- The Offshore Chemical Notification Scheme (OCNS) that manages chemical use and discharge by the United Kingdom (UK) and Netherlands offshore petroleum industries.
- The European Union legislation regarding the Environmental Impact Assessment (EIA) that requires a comprehensive assessment of the effects of projects on the environment.

An outcome of these initiatives was a regulation that prohibited the discharge of cuttings generated from drilling with synthetic- (i.e. oil/diesel) based drilling fluids where the synthetic oil on the cuttings is greater than 1% [63]. Additionally, the UK government proposed to phase out the discharge of cuttings contaminated with additional chemicals by December 31, 2000 [64]. Since oil-based muds that are often used currently must be 'skipped and shipped' (i.e. containerized and transported back to land for disposal) due to these environmental regulations, there is an effort within the industry to develop 'environmentally-friendly' chemical additives that work as well as the traditional chemicals.

It should be noted that in 2001, the USEPA published effluent limitations and guidelines, primarily applicable to offshore operations, on the discharge of synthetic-based drilling fluids (SBFs) from oil and gas drilling operations into waters of the United States.

### **6.3.2 Environmental Coordination in Europe**

The Convention for the Protection of the Marine Environment of the North-East Atlantic (known as the "OSPAR Convention") is the basis for national laws governing the discharge of offshore drilling wastes in the waters of the fifteen OSPAR signatory states [65, 33, 84]. The effort started in 1972 with the Oslo Convention against dumping; then, in 1974, the efforts were broadened by the Paris Convention to cover land-based sources and the offshore industry. These two conventions were unified, updated and extended by the 1992 OSPAR Convention.

The Paris Commission facilitated a thorough review of the use and manufacture of additives in order to establish the best environmental practice or best available techniques to prevent pollution [65]. The OSPAR list of substances that may be used or discharged offshore which are considered by OSPAR to Pose Little or No Risk to the Environment (PLONOR) contains substances whose use or discharge offshore are subject to expert judgment by the competent national authorities or do not need to be strongly regulated. The list of these chemicals may be found at [http://www.ospar.org/documents/dbase/decrecs/agreements/04-10\\_plonor%202008%20revision.doc](http://www.ospar.org/documents/dbase/decrecs/agreements/04-10_plonor%202008%20revision.doc).



The “main environmental acceptability criterion” for the UK government’s decision was biodegradation [64], which is consistent with Principle 10 of the Twelve Principles of Green Chemistry [66] adopted by the USEPA as part of its Green Chemistry initiative. In the Norwegian sector of the North Sea, chemical products must pass biodegradation, bioaccumulation, toxicity, and taint tests in order to be permitted for use [67]. Organisation for Economic Co-Operation and Development (OECD) North Sea countries require chemicals to be tested for ecotoxicity, biodegradation, and bio-concentration/bioaccumulation [64, 65].

### 6.3.2.1 Offshore Chemical Notification Scheme (OCNS)

The Offshore Chemical Notification Scheme (OCNS) manages chemical use and discharge by the UK and Netherlands offshore petroleum industries [68]. OCNS classifies chemicals using test protocols approved by OSPAR Harmonised Offshore Chemical Notification Format (HOCNF) coordinates the testing requirements for oilfield chemicals throughout the Northeast Atlantic sector.

To assess the potential environmental hazard associated with chemical products that may be used in offshore drilling operations, OCNS uses toxicity, biodegradation and bioaccumulation data for each chemical to calculate the ratio of Predicted Effect Concentration (PEC) against No Effect Concentration (NEC), and publishes the ratio as the Hazard Quotient (HQ). HQ is then used to rank products. Several lists of approved products that may be used for Production, Completion / Workover, Drilling or Cementing, ranked by their HQ may be found at [http://www.cefas.co.uk/offshore-chemical-notification-scheme-\(ocns\)/hazard-assessment.aspx](http://www.cefas.co.uk/offshore-chemical-notification-scheme-(ocns)/hazard-assessment.aspx).


In the UK, OCNS is regulated by the Department of Energy and Climate Change (DECC) with scientific and environmental input from the Centre for Environment, Fisheries and Aquaculture Science (Cefas) and the Fisheries Research Services (FRS). In the Netherlands, OCNS is regulated by the State Supervision of Mines (SSM) with scientific and environmental advice from Cefas and Netherlands government agencies [69].

#### 6.3.1.1 Cefas

Cefas assigns product ratings for additives used by the petroleum industry based on the physical, chemical and ecotoxicological properties of products. The assigned hazard groups vary from category A (most hazardous) through E (least hazardous), and HQ color from purple (most hazardous), through orange, blue, white, and silver, to gold (least hazardous) [70].

$$\text{Hazard Quotient (HQ)} = \frac{\text{Predicted Effect Concentration}}{\text{No Effect Concentration}}$$

**Table 6-1 - Cefas Chemicals Categories based on Hazard Quotient (HQ)**

Minimum HQ	Maximum HQ	Category	
>0	<1	Gold	Hazard Level Increases 
>=1	<30	Silver	
>=30	<100	White	
>=100	<300	Blue	
>=300	<1000	Orange	
>=1000		Purple	

Several of the product names provided to NYSDEC by operators on the Marcellus Shale are on the OCNS; the OCNS-approved product list and may be found at [http://www.cefas.co.uk/offshore-chemical-notification-scheme-\(ocns\)/hazard-assessment.aspx](http://www.cefas.co.uk/offshore-chemical-notification-scheme-(ocns)/hazard-assessment.aspx). OCNS-approved products that were also submitted for approval to NYSDEC are not cross-referenced here.

**6.3.2.2 Products Approved by Norway**

Norway is considered to have the most stringent regulatory environment among the OSPAR countries. Norwegian State Pollution Control Authority (SFT) also regulates the use of drilling muds through discharge permits. SFT assesses water-based fluids using data on bio-accumulation potential and bio-degradability. SFT encourages limiting use and discharges of even these approved products. Discharge of unused chemicals into the sea is forbidden [71].

**6.3.3 Environmental Coordination in Canada**

Canada-Newfoundland and Labrador Offshore Petroleum Board (C-NLOPB) in Canada utilizes a system called Offshore Chemical Selection Guidelines for Drilling & Production Activities on Frontier Lands. C-NLOPB follows the OCNS to a great extent.

**6.4 Summary**

The ‘environmentally-friendly’ aspect of hydraulic fracturing of deep shale formations presently stem from drilling techniques, like horizontal drilling and mutli-well pads with smaller overall footprint, and from the use of environmentally-friendly chemicals.

Several US-based chemicals suppliers advertise ‘green’ chemicals, but there does not seem to be a US-based metric to evaluate the environmental-friendliness of these chemicals.

In the North Sea area, several countries have established criteria that define environmental-friendliness, and utilize models and databases to track chemicals' overall hazardousness against those criteria. Similar to NYSDEC, the regulatory authorities in Europe request proprietary information from chemicals suppliers, and do not release any proprietary information into the public domain. The proprietary recipes for chemical additives are used to assess their potential hazard to the environment, and regulate their use as necessary.

If applicable, New York could choose to evaluate the criteria used in Europe or the US might choose to set up an independent scientific entity to evaluate all chemicals proposed for use within US territories. However, at this time, it may not be feasible to require the use of 'green' chemicals because presently there is no metric or chemicals approvals process in place in the US. The evaluation of the 'greenness' of a chemical needs to consider the life-cycle impacts associated with that chemicals; and setting up a metric that provides a comprehensive evaluation is difficult.

It is important to note that several products manufactured by US-based companies, and used or proposed for use in the Marcellus Shale in New York, may be found in the European approved chemicals lists.

## **7 ALTERNATE WATER SOURCES FOR HYDRAULIC FRACTURING OPERATIONS**

### **7.1 Introduction**

Hydraulic fracturing operations require the use of large quantities of water. Data from the Marcellus Shale operations indicate that typical usage is approximately 1 million gallons (MG) for a vertical well and between 2.5 and 3.5 MG for a horizontal well, with maximum usage up to 6 MG.

The water sources that are used initially are those that are the most readily accessible at a reasonable cost. These sources tend to be municipal (potable) water, surface water, and groundwater. Utilizing potable water is more costly and subject to quantity limitations; utilizing fresh surface water or groundwater may be less costly but may deplete limited fresh water resources, may not be available for withdrawal at the rate needed at all times, may be subject to restrictions on interbasin transfers, and may have quality concerns (e.g., affected by abandoned mine drainage). Using alternate water sources may be beneficial in replacing or supplementing the more conventional sources.

### **7.2 Potential Alternate Water Sources**

Alternate hydraulic fracturing water sources that should be considered, where available, include:

- Effluent from municipal or industrial wastewater treatment plants
- Partial re-use of fracturing water (discussed in Section 5)
- Non-contact cooling water discharges from industrial plants
- Saline aquifers
- Stormwater ponds
- Impoundments (lakes, reservoirs, quarries)
- Mine discharges
- Deep mine pools

Alternate water sources need to meet a number of criteria before they may be considered for hydraulic fracturing, as discussed below.

### **7.3 Factors that Affect Usability of Alternate Water Sources**

Operators should consider several factors when evaluating the usability of any particular water source. Decisions regarding use vs. non-use could change with time depending on innovations in technology and other competing uses for water. Factors affecting usability include:

Availability – The “owner” of the source needs to be identified, contact made, and agreements negotiated.

Distance/route from the source to the point of use – The costs of trucking large quantities of water increases and water supply efficiency decreases when longer distances and travel times are involved. Also, the selected routes need to consider roadway wear, bridge weight limits, local zoning limits, impacts on residents, and related traffic concerns.

Available quantity – Fewer larger water sources avoids the need to utilize multiple smaller sources.

Reliability – A source that is less prone to supply fluctuations or periods of unavailability would be more highly valued than an intermittent and less steady source.

Accessibility – Water from deep mines and saline aquifers may be more difficult to access than a surface water source unless adequate infrastructure is in place. Access to a municipal or industrial plant or reservoir may be inconvenient due to security or other concerns. Access to a stream may be difficult due to terrain, competing land uses, or other issues.

Quality of water – The fracturing fluid serves a very specific purpose at different stages of the fracturing process. The composition of the water could affect the efficacy of the additives and equipment used. The water may require pre-treatment or additional additives may be needed to overcome problematic characteristics.

Potential concerns with water quality include scaling from precipitation of barium sulfate and calcium sulfate [1]; high concentrations of chlorides, which could increase the need for friction reducers; very high or low pH (e.g. water from mines); high concentrations of iron (water from quarries or mines) which could potentially plug fractures [1]; microbes that can accelerate corrosion, scaling or other gas production [6]; and high concentrations of sulfur (e.g. water from flue gas desulfurization impoundments), which could contaminate natural gas. In addition, water sources of variable quality could present difficulties.

Similar to reusing or recycling flowback for hydraulic fracturing, experts on hydraulic fracturing agree that high quality water is easy and convenient to use, and that somewhat lower quality water may also be utilizable for hydraulic fracturing [1]. Perhaps due to the additional cost and inconvenience of withdrawing and transporting alternate water sources, expectations of water quality are higher of alternate water sources than of recycled flowback. Based on the applicable water quality specifications, several of the alternate water sources identified in Section 7.2 (such as flowback, saline aquifers, mine discharges and deep mine pools) may be usable only after appropriate treatment.

Permittability – Applicable permits and approvals would need to be identified and assessed as to feasibility and schedule for obtaining approvals, conditions and limitations on approval that could impact the activity or require mitigation, and initial and ongoing fees and charges. Preliminary discussions with regulating authorities would be prudent to identify fatal flaws or obstacles.

Disposal – Proper disposal of flowback from hydraulic fracturing will be necessary, or appropriate treatment for re-use provided. Utilizing an alternate source with sub-standard quality water could add to treatment and disposal costs.

Cost – Sources that have a higher associated cost to acquire, treat, transport, permit, access or dispose, typically will be less desirable by industry.

## **7.4 Summary**

Theoretically, any water source may be utilized for hydraulic fracturing. But in practice, several factors could affect the usability and suitability of these sources. The perceptions of usability and suitability would likely change with time based on the value of natural gas recovered, innovations in technology related to water treatment, regulations, and costs. Each service company and operation would need to evaluate local conditions to determine the availability of alternate water sources to a particular gas well.

## **8 WATER WELL SAMPLING NEEDS**

### **8.1 Introduction**

Based on experiences in other states, there is concern that high-volume hydraulic fracturing operations may impact private water wells in the State of New York (the State) by contaminating the water well or depleting the resource [72, 73, 75]. However, the USEPA found no threat to water sources from hydraulic fracturing [75, 76]. Additionally, Interstate Oil and Gas Compact Commission (IOGCC) member states have all stated that there have been no cases where hydraulic fracturing has been verified to have contaminated drinking water [76]. This section summarizes available information on private water well sampling, testing, and monitoring activities performed in a number of states in conjunction with hydraulic fracturing of deep shale formations. The desktop research identified relevant information for New York, Pennsylvania, Ohio, Kentucky and Texas.

This section also proposes ‘indicator’ compounds/elements to monitor before and after drilling/fracturing to indicate whether there may be a connection between private water well contamination and hydraulic fracturing operations. These indicators have been selected using limited analytical results of flowback from the Marcellus Shale from operations in New York and Pennsylvania.

### **8.2 Water Well Sampling Requirements in Pennsylvania**

Section 208 of Pennsylvania’s Oil and Gas Act - Protection of water supplies – requires ‘any well operator who affects a public or private water supply by pollution or diminution [to] restore or replace the affected supply with an alternate source of water adequate in quantity or quality for the purposes served by the supply’ [77].

The gas well operator may be held responsible for any drinking water well supply contamination or reduction within 1,000 feet of the gas well that is discovered within 6 months of gas well completion [7]. Pre-drilling monitoring of water wells within 1,000 feet of the gas well may, therefore, be driven by both the drinking water supply owner and the gas well operator, at the gas well operator’s expense. Post-drilling water supply well monitoring by the well operator is presently not required in Pennsylvania. While the drinking water well owner may use a ‘Do-it-yourself’ sampling kit, a state-certified laboratory needs to perform the analyses if legal action were later required based on the analytical results.

### **8.3 Water Well Sampling Requirements in Ohio**

The Ohio Department of Natural Resources administers a pre-drilling water sampling program in Ohio. This program requires gas well operators to prepare a sampling plan; the actual sampling requirements are determined on a case-by-case basis and may be contingent on a variety of factors, including hydrology, geology, and aquifer characteristics. The program may require the gas well operator to sample all domestic water supply wells in a given area; the actual size of the sampling area varies by operation.

The State of Ohio requires analyses of the following parameters to characterize pre-drilling water quality: alkalinity, barium, calcium, chloride, conductivity, iron, magnesium, pH, potassium, sodium, sulfate, and total dissolved solids (TDS) [78].

#### **8.4 Water Well Sampling Requirements in Texas**

The Railroad Commission of Texas has rules in place to protect groundwater and surface water resources in Texas. Texas Administrative Code Title 16 Economic Regulation, Part 1- Railroad Commission of Texas, Chapter 3 Oil and Gas Division, Rule §3.8 Water Protection provides guidance on anti-degradation. Specific information or guidance on water supply well protection was not readily found.

#### **8.5 Water Well Sampling Requirements in Kentucky**

The Kentucky Department of Environmental Protection's Division of Water does "not regulate contaminants in private wells" [79]. Kentucky Administrative Regulations have general requirements and guidelines for groundwater protection, but the desktop search did not find any specific water supply monitoring requirements associated with natural gas drilling in the Devonian Shale [80].

#### **8.6 Existing Water Well Protection in New York**

Article 23, Title 3 of the Environmental Conservation Law (ECL) authorizes the New York State Department of Environmental Conservation (NYSDEC) to require that oil or gas wells be drilled, constructed, operated and plugged, and the surrounding land reclaimed, to prevent or remedy "the escape of oil, gas, brine or water out of one stratum into another" and "the pollution of freshwater supplies by oil, gas, salt water or other contaminants" [81].

NYSDEC requires a full environmental assessment if a proposed oil or gas well is within 2,000 feet of a municipal well and a supplemental Environmental Impact Statement if the proposed oil or gas well is within 1,000 feet. Strict oil or gas well construction requirements are expected to protect all groundwater resources, including private wells [82].

#### **8.7 Enhanced Water Well Protection in New York**

NYSDEC appears to have a comprehensive program in place to protect municipal wells in the State, while protection of private water supply wells is based on gas well construction requirements. The State could potentially enhance its protection of private water well supplies by implementing the following:

- NYSDEC may be able to draw from Ohio's requirements and enhance the State's requirements by providing to potential gas well operators a succinct list of parameters



to monitor, at the producer's expense, in private water wells within a certain distance of a proposed gas well, before and after a fracturing operation.

- NYSDEC could draw from Pennsylvania's requirements and require any gas well operator who affects the quantity or quality of a private water supply to restore or replace, within a reasonable timeframe, the affected private water supply with an alternate source of water similar in quantity and quality to the original supply.

## **8.8 Indicator Compounds/Elements of Potential Contamination due to Hydraulic Fracturing**

Limited time-series data of flowback from Marcellus Shale gas wells in Pennsylvania show that concentrations of several parameters in flowback increased over the 2 to 3 week period. These parameters include: TDS, hardness, calcium, magnesium, bromide, chloride, fluoride, chemical oxygen demand, barium, and manganese. Concentrations of sulfates, bicarbonates, total Kjeldahl nitrogen, 5-day biological oxygen demand, phosphorus and alkalinity decreased with time, likely due to additives used.

Literature based on flowback data from other shale formations indicates that the concentrations of chlorides and TDS (likely heavily influenced by chlorides) increase over the flowback period; literature based on flowback data from the Marcellus indicates that the concentrations of TDS and barium increase over the flowback period. While other parameters may be influenced by mobilization of materials in the shale formation or due to fracturing fluids, there is insufficient data at this time to make a definitive determination that these other parameters would always be found primarily/exclusively due to fracturing operations in the Marcellus Shale area.

In order to determine if a private water supply well has been contaminated due to hydraulic fracturing operations, comprehensive pre- and post-drilling water quality monitoring may be warranted<sup>39</sup>. Such monitoring may be costly, though.

Monitoring for parameters such as barium, TDS and pH could indicate if the private water well has been contaminated due to the fracturing operation. Monitoring for strontium, sodium, chloride, hardness (calcium and magnesium), surfactants, total suspended solids (TSS), iron, carbonates and bicarbonates could provide a better understanding of the extent of potential contamination [7].

Diesel is no longer used in fracturing operations, but is used to fuel equipment. Therefore, sampling for benzene, which is contained in diesel, could indicate above ground spills.

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<sup>39</sup> Many water wells in New York are completed in shale formations. Based on NYSDEC's experience with investigating water well complaints, pre-drilling private water well quality may vary due to impact of even an undeveloped shale.

Monitoring for methane would alert potential uncontrolled emissions due to damaged casings, etc. It has also been suggested that an isotopic analysis of carbon in methane could determine if the gas is from a shallow source or from a deep reservoir.

## **8.9 Summary**

There is concern among the public, particularly among property owners and private water supply well owners near hydraulic fracturing operations, about potential well water contamination due to fracturing operations. This section surveyed existing private water well sampling, testing and monitoring requirements in New York, Pennsylvania, Ohio, Kentucky and Texas.

Barium and TDS are recommended as indicator substances to monitor for, at a minimum, in private water supply wells, before and after gas well drilling/fracturing to determine potential contamination from the operation. Private water well quality depends on a number of factors, including water well construction, potential pre-existing contamination, and natural water quantity variations. Therefore, establishing pre-drilling well water conditions is important to determine the potential impact of the fracturing operation.

The frequency and length of monitoring would likely depend on the specific location; but may be pre-drilling, then once per month from the start of operations until six months after completing fracturing operations; and then once per six months until the well is plugged. As with other water-quality-related permits, the frequency may be reduced if the operator maintains its record of compliance. Monitoring for additional parameters like pH, strontium, sodium, chloride, calcium, magnesium, surfactants, TSS, iron, carbonates, bicarbonates and diesel would provide a better understanding of potential contamination of private water well supplies due to hydraulic fracturing operations or above ground spills.

## **9 SUMMARY AND CLOSING**

The process of horizontal drilling and high-volume hydraulic fracturing uses large volumes of water with small concentrations of chemical additives to assist and enhance drilling and fracturing. A portion of the fracturing fluids returns to the surface as flowback. This fluid contains variations of additives, parameters that were present in the source water, new compounds formed due to reactions between additives and substances mobilized within the shale formation.

There is concern among the public that the chemical additives used for fracturing or flowback fluid could contaminate some of the State's water resources and, as a result, interfere with the use of those sources in accordance with their designated use classifications. This study addresses this issue, subject to the limited amount of data available for evaluation.

### **9.1 Summary**

Section 2 presents 13 classes of chemical additives that may potentially be used in hydraulic fracturing operations and, based on proprietary information and MSDS received from service companies and operators via the NYSDEC, presents a list of basic compounds and elements found in approximately 230 products used or proposed for use in hydraulic fracturing operations in New York.

Section 3 discusses volumes and composition of flowback based on publicly available literature and data from well operators, and trends in volume and composition observed based on information from one well operator. This section includes a summary of the Marcellus Shale Coalition Study Report. It also presents a list of compounds and elements based on analytical results of flowback from the Marcellus Shale.

Section 4 surveys the sufficiency of federal and New York State regulations and guidelines to protect water resources in the State. This section provides a preliminary comparison of constituents found in additives (in Section 2) and flowback (in Section 3) with contaminants/pollutants regulated by the federal drinking water standards, the SPDES program, NYSDOH's POC and UOC Standards, or which have guidance through TOGS111. Nearly all the parameters detected in laboratory analyses provided by industry appear to be addressed in Federal or State regulations or guidances.

Section 5 is a preliminary survey of flowback recycling and on-site treatment technologies currently used to a limited extent for other drilling/fracturing operations. On-site treatment of flowback is costly, and technology is not widely available for use in the Marcellus Shale. However, these technologies are evolving to meet industry needs and regulatory requirements. At the present time, operators appear to recycle flowback more than treat it.

Section 6 surveyed 'environmentally-friendly' hydraulic fracturing technologies and chemicals. It appears that environmentally-friendly technologies are in experimental phases or have only been used under conditions different from the Marcellus. The 'environmentally-

friendly’ aspect of hydraulic fracturing of deep shale formations presently stems from drilling techniques, such as horizontal drilling and multi-well pads with smaller overall footprint, and from the use of environmentally-friendly chemicals. While there are inferences to green or environmentally-friendly chemicals and technologies, their lifecycle environmental performance has not yet been evaluated.

There is multinational cooperation in Europe regarding oil and gas drilling in the North Sea. This study did not evaluate the robustness or efficacy of European efforts, but suggests that the OSPAR Convention and the Offshore Chemical Notification Scheme (OCNS) serve as the starting point for setting up a framework in New York State (or the US<sup>40</sup>) to promote environmentally-conscious hydraulic fracturing operations. The specific concerns associated with onshore vs. offshore operations would likely be different, but the framework, approach and lessons learned from offshore operations would likely be applicable at onshore operations as well.

Section 7 is a survey of alternate water sources that may be utilized for hydraulic fracturing operations. Several alternate sources might potentially be available in New York, but they are not well-bore-ready. Each alternate source has its limitations. Effluent from wastewater treatment plants or non-contact once-through cooling water discharge from industrial facilities may presently be a significant component of a waterbody<sup>41</sup>, and its use would likely require approvals and permit modifications from waterbody commissions or other agencies. Water from saline aquifers, quarries, or mines would likely require significant treatment. These sources already contain high concentrations of TDS – the parameter likely of greatest operational concern in flowback. Treatment is costly. Innovations in treatment technologies and potential use of alternate water sources would likely depend on the value of natural gas that may be harvested from the Marcellus, the availability, costs and other competing uses of freshwater in the general area, and regulations and guidelines on withdrawal, use, consumption, treatment and disposal (i.e. the complete life-cycle) of water used in hydraulic fracturing.

There is concern that hydraulic fracturing operations may contaminate private water wells in the vicinity. Section 8 surveys efforts in Pennsylvania and Ohio to potentially preserve water quality and quantity in private water wells. NYSDEC has the authority to protect water resources in the State, and has a comprehensive program to protect municipal water wells. Section 8 draws from experiences and guidelines in Pennsylvania and Ohio to suggest enhancements to water resource protection (particularly private water well supplies) in the State. In addition, based on analytical results of flowback from the Marcellus obtained from operators and published literature, Section 8 suggests a series of parameters to test and monitor for in private well water before and after drilling/fracturing a gas well.

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<sup>40</sup> The USEPA has initiated a study on hydraulic fracturing.

<sup>41</sup> Particularly during low flow period, the relatively consistent discharge rate from POTWs is important to maintain minimum flow rates in small waterbodies.

## 9.2 Limitations of the Survey

This study looked at a variety of subjects associated with hydraulic fracturing within a very short period of time. The information is based on limited interactions with service companies, telephone interviews and articles from industry experts, or information published on websites, and is not based exclusively on peer-reviewed published literature. Composition of additives and analytical results of flowback are from service companies and operators who voluntarily shared proprietary information with NYSDEC. Such information was used in this study under a strict confidentiality agreement. The level of detail of information and data from different sources is not consistent. Given these study conditions, information presented in this report may be refined in the future as more information becomes available.

This study likely captures all the classes of chemical additives used in fracturing operations. As additional service companies, operators and chemicals suppliers share more information, the table with basic constituents in additives (Table 3-1) may be further expanded.

Except for the analytical results provided by the MSC, the different analyses of flowback data tested for different sets of parameters. In addition, different detection methods (which have different detection limits) have been used to test for the same parameter. All operators testing and reporting concentrations for the same comprehensive list of parameters, guidelines on allowable detection methods under different conditions, along with the composition and quantity of water and additives used would provide a better understanding of constituents in flowback. Flowback composition changes with time. All operators monitoring flowback at several pre-specified points in time would also improve understanding of flowback.

On-site treatment and recycling are in pilot phases, and much of the information is presently considered to be proprietary. Incentives to innovate and share information would help understand the industry's progress in on-site treatment and recycling.

Some US-based companies advertise 'green' chemicals. But there does not appear to be a common metric in place to evaluate environmental-friendliness in the US. New York State may be able to draw from experiences in Europe and formulate a metric to objectively measure the environmental-friendliness of chemicals or technologies so the industry has a specific goal to work towards, and the environmental impact of hydraulic fracturing may be measured more objectively. Significant differences between European countries and the US include the size, the state-based governance system, and offshore vs. onshore operations. European countries are smaller than the US and most environmental regulations and requirements apply to the entire country, while in the US regulations and requirements are often administered at the state-level. It is imperative that these regulations and requirements continue to be administered at the state-level. Interstate collaboration with respect to shale development similar to riverbasin commissions would likely be beneficial.

This study suggests a few parameters to test and monitor for in private water wells before and after drilling a gas well in the vicinity. A pilot study to evaluate the appropriateness of these parameters may lend greater credibility to the perceived need for a State-wide private well testing program.

### **9.3 Closing**

The oil and gas industry has developed innovative technologies to harness natural gas from the low-permeability Marcellus Shale formation at depths of several thousand feet. Adequate safeguards are necessary to carry out these drilling and fracturing operations in an environmentally sensitive manner. The industry has shared proprietary information and experiences regarding hydraulic fracturing operations which have been utilized in this report.

As with other states in the core Marcellus Shale region, New York State is tasked with promoting efforts to develop natural gas resources in support of federal and state energy policies while protecting and preserving other important resources of the State. This balance is reflected in the laws and regulations that have been promulgated to address public needs for energy and environmental health.

Natural gas harvesting from the Marcellus Shale provides an opportunity for agencies, industry and the public to work together to develop one resource while protecting and preserving other resources and respecting the competing public demands on the State.

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