

# Chemicals



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## **Marcellus Shale Wastewater Issues in Pennsylvania— Current and Emerging Treatment and Disposal Technologies**

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### **Introduction**

Over the last few years the exploration and development of the Marcellus shale has rapidly escalated in some regions of Pennsylvania, but the capacity for treating and disposing of the drilling wastewater has lagged. Several factors contribute to the challenge of finding the best solutions for managing Marcellus wastewater:

- rapid expansion of the industry in Pennsylvania outside of traditional gas drilling areas, where treatment infrastructure is currently limited,
- concentration and range of pollutants in waste fluids,
- variability of wastewater chemistry in time and space,
- volume of waste fluids,
- limited assimilative capacity<sup>1</sup> of streams, and
- lack of traditional options for treatment/disposal.

However, over the past two years or so, the available technology and the regulatory climate for Marcellus wastewater treatment have been changing rapidly in response to the discovery of economically feasible amounts of extractable shale gas. Marcellus wastewater treatment options are likely to continue changing quickly for the next few years. With the recent finalization of two important regulatory changes (see pages 3 and 7), many experts expect a more stable regulatory climate during that time.

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<sup>1</sup>Capacity of a water body to receive wastewater or other pollutants without harmful effects on aquatic life or reducing humans' ability to enjoy benefits from use of the water body.

### **The Volume of Wastewater Generated by Marcellus Drilling in Pennsylvania**

The Penn State Marcellus Center for Outreach and Research has verified estimates are that we will see about one well pad per square mile in those areas deemed to have economically recoverable volumes of natural gas, with six to ten wells per pad. The Susquehanna River Basin Commission estimates that 72 percent of the 27,510-square-mile Susquehanna River basin (Pennsylvania and New York) is underlain by the Marcellus shale, but much of this area is outside of the portion of the Marcellus considered to be economically recoverable. The gas industry drilled 1,386 Marcellus wells in 2010, compared to 763 in 2009.

Marcellus shale wells require a large quantity of water to aid in the extraction of natural gas. Hydrofracturing ("fracking") (for background on hydrofracturing, see [extension.psu.edu/water/marcellus-shale/introduction-to-hydrofracturing/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/introduction-to-hydrofracturing/at_download/file)) a horizontal Marcellus well may use three to eight million gallons of water, typically within about one week. Various sources show that much of the water used remains deep underground, but the approximately ten percent that resurfaces in the subsequent 30 days amounts to about 300,000 to 800,000 gallons of wastewater per well drilled.

Data that the gas industry reported to the Pennsylvania Department of Environmental Protection (DEP) show that the industry produced

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about 235 million gallons of wastewater in the second half of 2010.

## Types and Chemistry of Marcellus Wastewater

The fluid that emerges from the top of a Marcellus well shortly after hydrofracturing (within ~30 days) is called *flowback water*. *Produced waters* surface along with the natural gas after the well is in production. We are concerned here mainly with flowback water, which is high in total dissolved solids (see TDS section), salts, and other parameters (Table 1) and may contain sand, heavy metals, oils, grease, manmade organic chemicals that aid in the fracking process, radioactivity from contact with radioactive rocks underground, or other unknown or trace contaminants. The untreated flowback water can not be discharged to Pennsylvania's streams, lakes, or rivers without undergoing

Parameter	Range	Median	Units
Total alkalinity	48.8 – 327	138	mg/L*
Hardness as CaCO <sub>3</sub>	5,100 – 55,000	17,700	mg/L
Total suspended solids	10.8 – 3,220	99	mg/L
Turbidity	2.3 – 1540	80	NTU†
Chloride	26,400 – 148,000	41,850	mg/L
Total dissolved solids	38,500 – 238,000	67,300	mg/L
Specific conductance	79,500 – 470,000	167,500	umhos/cm‡
Total Kjeldahl nitrogen	38 – 204	86.1	mg/L
Ammonia nitrogen	29.4 – 199	71.2	mg/L
Biochemical oxygen demand	37.1 – 1,950	144	mg/L
Chemical oxygen demand	195 – 17,700	4,870	mg/L
Total organic carbon	3.7 – 388	62.8	mg/L
Dissolved organic carbon	30.7 – 501	114	mg/L
Bromide	185 – 1,190	445	mg/L

treatment. Untreated flowback water is toxic to aquatic life, particularly trout and other sensitive species.

## Fracking Additives

Sand and chemicals are added to water used for hydrofracturing to facilitate gas extraction. Range Resources Corporation in summer 2010 became the first gas company active in the Marcellus shale to disclose which chemicals their company uses in fracking and at what amounts. For example, to frack a well in southwest Pennsylvania, Range Resources reported using:

- 3.81 million gallons of water
- 4.57 million pounds of sand
- 1,333 gallons of hydrochloric acid
- 1,695 gallons of a friction reducer
- 2,211 gallons of an antimicrobial agent and
- 386 gallons of a scale inhibitor (which includes ethylene glycol, a component of antifreeze).

There is concern about some of these chemicals, but the industry points out that they total less than 0.5 percent of the total fracking fluid injected into the well. Some experts have noted a decline in the use of scale inhibitors, because scale has been less of a problem than anticipated.

## Total Dissolved Solids: What Is It and Why Does It Matter?

As noted above, the main problem with flowback water is extremely high levels of total dissolved solids (TDS). TDS is a measure of dissolved matter (salts, organic matter, minerals, etc.) in water. Inorganic constituents (for Marcellus wastewater, mostly sodium, calcium, and chloride picked up from the rock formation) contribute most of the

**Table 1: Summary of selected chemical parameters of concern in flowback water sampled 14 days after well fracking.** Adapted from data of Hayes, T. 2009. Sampling and analysis of water streams associated with the development of Marcellus shale gas. Final report to Marcellus Shale Coalition. Gas Technology Institute, Des Plaines, IL.

\* milligrams per liter | † nephelometric turbidity units | ‡ micro mhos per centimeter



total concentration of TDS. TDS can be naturally present in water or the result of mining, other types of oil and gas extraction, steel and pharmaceuticals manufacturing, some power plants, and others.

Under the Federal Safe Drinking Water Act, the U.S. Environmental Protection Agency (US EPA) classifies TDS as a secondary maximum contaminant level (sMCL). This means that there is a recommended maximum level of 500 mg/L, but no requirement that public water systems meet this level. Under the Pennsylvania Safe Drinking Water Act and associated regulations, however, secondary standards are enforceable. TDS is not expected to harm human health at the sMCL, although it may negatively affect water's taste. But elevated TDS levels may damage water treatment equipment or reduce the effectiveness of treatment for other contaminants. However, TDS is of particular concern to in-stream aquatic health, because at certain levels it becomes toxic to aquatic life, increasing the salinity in freshwater systems and changing the composition of the water. Some constituents that are a part of the TDS measurement, such as arsenic, lead, and nitrate, can have health effects if they exceed drinking water standards.

In 2010 the Pennsylvania Department of Environmental Protection finalized new regulations to protect Pennsylvania's streams, rivers, lakes, and public drinking water by limiting the amount of total dissolved solids that could be discharged into waterways. These regulations were a major step in reducing the uncertainty of Marcellus wastewater treatment in the future by defining one important standard that treated wastewater must attain before discharge. Many experts feel that the existence of a clear standard now will foster innovation in the field of Marcellus wastewater treatment.

DEP developed the new TDS standard for several reasons:

- Some of the state's waterways have limited capacity to assimilate additional TDS and sulfates.
- The Marcellus shale natural gas industry is expanding rapidly in Pennsylvania. Many of the areas where Marcellus drilling is prevalent also are affected by acidic mine drainage from coal mines, which itself can elevate dissolved solids in waterways.
- Because of the difficulty of pinpointing pollution sources in the face of water quality problems and the many industrial sectors whose wastewaters can be high in TDS, establishing an across-the-board effluent (wastewater that has been treated and is ready for discharge to natural waters) limit for TDS levels the playing field.
- Extensive new treatment capacity needs are expected beyond the current limited options for treatment and disposal.

### **Recent TDS Regulations Apply to New Dedicated Treatment Facilities**

The new regulations establish an effluent standard for high-TDS wastewater from most industrial sectors of 2,000 mg/L. A tighter standard of 500 mg/L for TDS, 250 mg/L for chlorides, 10 mg/L for barium, and 10 mg/L for strontium applies to wastewater from the natural gas industry because of its much higher initial concentrations and overall loadings. These four standards are based on monthly averages. The regulations exempt TDS loads authorized prior to August 21, 2010, when the regulations took effect. The final regulations also exempt some specific TDS loads and allow for more or less stringent standards based on a watershed's ability to assimilate TDS.

The regulations apply to new or expanded TDS loads at facilities treating TDS wastewater in Pennsylvania. Existing discharge loads of TDS are exempt from the regulation unless or until treatment facilities wish to expand.

DEP estimates that it will cost between \$0.12 and \$0.25 per gallon to treat TDS wastewater originating from the natural gas industry. This is expensive compared to municipal wastewater treatment (pennies per gallon), but treatment costs are expected to be miniscule in light of the industry's expected annual revenue in the Pennsylvania. Industry observers also note that treatment costs are likely to come down as competition between processes and providers increases and more treatment facilities come on line. This should begin in earnest now that the new TDS regulations specifically identify the standards the treatment industry will have to meet.

**Table 2: Treatment/disposal options for flowback water in Pennsylvania and their relative advantages and disadvantages.**  
Adapted from Yoxheimer, D. Water use and water reuse/recycling in Marcellus shale gas exploration and production. 2010. Penn State College of Agricultural Sciences, Cooperative Extension, Marcellus Shale Educational Webinar Series. Oct. 21. [tinyurl.com/24o4kra](http://tinyurl.com/24o4kra).

Treatment	Advantages	Disadvantages
Dilution at publicly owned sewage treatment plant or an existing, dedicated brine treatment plant	Minimal cost	Limited capacity now that DEP TDS regulations are in effect  Potential to upset the sewage treatment process  Does not ensure protection of downstream public water supplies
Treatment at a new, dedicated brine treatment plant	Meets August 2010 DEP TDS regulations  Protects downstream PWS intakes  Ensures available assimilative capacity for other industries	Limited current capacity  Potentially high transportation costs  Higher treatment costs than simple dilution
Direct reuse without treatment (blending of flowback with freshwater for reuse)	Minimal cost	Some potential for well plugging because of high total dissolved solids and sand in the water
On-site treatment and reuse (recondition water through treatment)	Minimal potential for well plugging	Moderate costs
Off-site treatment and reuse	Minimal potential for well plugging	High transportation costs
Off-site disposal via deep underground injection	No discharge to a stream	High transportation costs

## Options for Flowback Water Treatment and Management

Extremely high TDS is the primary reason that Marcellus flowback water requires the development of new treatment methods. Table 2 summarizes the current treatment/disposal options and their advantages and disadvantages.

### Dilution at Publicly Owned Sewage Treatment Facility

Traditional treatment at publicly owned sewage treatment plants offers only dilution of TDS, rather than removal, and the end result is the discharge of salty water into surface waters. It is inexpensive (pennies per gallon) and often fairly convenient. In the very early phase of development of the Marcellus field in 2007 and 2008, dilution was a fairly common disposal method, but DEP soon realized that streams couldn't continue to assimilate the necessary level and volume of TDS and has

since finalized new effluent standards for TDS wastewaters, as discussed above. As of April 2011, only 15 sewage treatment plants statewide were accepting flowback water, and only as a small percentage of their total daily intake. That same month, DEP asked drilling companies to stop bringing frack water for treatment at these facilities because of mounting water quality concerns.

### **Existing Dedicated Treatment Facilities**

As with treatment at publicly owned sewage treatment plants, the existing, dedicated brine treatment facilities offer only dilution of TDS, rather than removal, and discharge salty water to surface water. For many years, these facilities have accepted and treated wastewater from the oil and gas industry in Pennsylvania, but the increased volumes and loads from Marcellus drilling mean that new facilities are needed to meet the gas industry's wastewater treatment needs. The final TDS regulations exempt 17 existing discharge loads. However, should one of these facilities decide to expand, the new treatment standards would apply to the expanded load.

### **New Dedicated Treatment Facilities**

Currently, there are twenty-five newly proposed dedicated treatment facilities (conventional brine plants) planning to treat natural gas wastewater so that it can be discharged to surface water. The equipment is designed to remove salts, metals, and oils. These facilities must meet the new TDS regulations. One of the drawbacks of dedicated treatment is location. Because of the high costs of transportation, it will be important to properly locate these facilities throughout the Marcellus region to minimize these costs.

### **Reuse With or Without Pretreatment**

Over the past few years, many gas companies began reusing some of the flowback water for other frack jobs, either with or without some level of treatment. Relatively clean initial flowback water (which returns to the land surface within a few days of fracking) can be blended without treatment with fresh water at the well pad and reused.

Remaining fluids may have some pretreatment done via an on-site "package" plant or via round-trip trucking to an advanced facility (see page 6). A package treatment plant is essentially a trailer equipped with a treatment system that can be transported and used from site to site to treat

the flowback water for reuse. An area of active research is how package plants will handle the large volume of water that is necessary to drilling operations. Pretreatment often involves filtering out sediment and removing barium, strontium, and other metals, but otherwise has little effect on the salts comprising the majority of TDS. Pretreatment on- or off-site may prepare the water for reuse or transportation for disposal or further treatment. Reuse and on-site treatment allow for reduced truck traffic and transportation expenses. No discharges are allowed from well sites to rivers or streams.

It is important to recognize that reusing flowback water concentrates contaminants. The water is reused a number of times in fracking until it contains approximately 50,000–100,000 mg/L TDS, at which point it is treated.

Several factors complicate on-site treatment: (i) the variability in flowback water chemistry over time since fracking, (ii) the variability in flowback water chemistry across the state, and (iii) the use of different amounts and types of frack additives by different companies and at different locations. Water reuse can also make it more difficult for gas companies to determine the needed amounts of frack additives.

For several reasons, it is currently difficult to estimate the amount of flowback water being reused. Act 15 was signed into law in March 2010, requiring Marcellus drilling companies to file biannual well and waste production reports with DEP. So the system for tracking these data is new and was designed to track wastewater, not recycling, and therefore needs to be improved and refined to better estimate flowback recycling volumes. Furthermore, additional resources may

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<sup>2</sup>About 70 percent of the waste fluid is labeled as going to "brine or industrial" treatment facilities. At least some of these facilities are explicitly set up to treat water and return it to the operators (the water trucks are full in both directions). This is reuse, but is not counted in the 17 percent figure.

need to be devoted to data processing at DEP, and there is inconsistency in how drilling companies self-report wastewater statistics and define recycling. Given these caveats, it seems that the industry recycled about 17 percent of all water used during the last six months of 2010. However, DEP and the industry currently cite the figure of 70 percent recycling because they define "recycling" differently.<sup>2</sup>

### Advanced Facilities

New technologies for treating Marcellus wastewater are currently an area of intense research. Most involve evaporation and crystallization of salts. GE and some other companies are developing mobile evaporator units. This kind of advanced treatment option could offer the advantages that the effluent meets new state standards and that the treated water is directly reusable in fracking other wells. Its big disadvantages include production of a large solid waste residue (salts) and high costs (about \$0.25 per gallon). The salts from advanced treatment facilities may find a beneficial use in road deicing or other uses.

DEP in October 2010 had issued three permits for TDS wastewater treatment facilities, two in Lycoming County and one in Somerset County, and had at least 25 other permit applications under review.

At least one treatment company, operating in Lycoming County, currently returns to each gas company the water they send in after it has been treated. This is accomplished via separate storage tanks. This provision of so-called "make-up water" as a cost-saving benefit of the process should reduce the need for water withdrawal permits.

One of the first facilities for treating flowback and produced water in the Marcellus shale area became operational in April 2010. As of September 2010 the facility had treated and returned to clients 12

million gallons for reuse in fracking. The company has an additional facility planned for Tioga County and two for Bradford County.

### Deep injection/disposal wells (Underground injection control)

Deep injection wells are a form of waste disposal that pumps untreated wastewater down through very deep wells and out into rocks bounded above by an impermeable rock layer(s). The U.S. Environmental Protection Agency (EPA) is responsible for permitting these wells in Pennsylvania.

Pennsylvania currently has about seven such brine disposal wells. Only one is a commercial well, and it has limited or no available capacity and is not permitted for Marcellus wastewater disposal. New York State has six brine disposal wells, West Virginia has 74, and Ohio has 159. Some Marcellus wastewater from Pennsylvania is currently trucked to these out-of-state locations, but transportation costs make this an expensive disposal option complicated by interbasin transfers of water.

Although Pennsylvania may eventually have additional deep injection wells for Marcellus wastewater, they are not expected to solve the problem, as they do in Texas, which has about 7,000 brine disposal wells. Deep injection wells are difficult and costly to permit, and relatively few locations in Pennsylvania have suitable geology. Another limitation is that old shallow oil and gas wells in the area of influence of any new deep injection wells would have to be plugged. Pennsylvania has thousands of old shallow oil and gas wells, so this would be a significant challenge.

According to 2010 DEP industry-reported records, almost 12 million gallons of Marcellus-derived fluids (an average of 32,620 gallons per day) were generated in Pennsylvania and treated and disposed of at the following Ohio facilities:



- underground injection wells: nearly 11 million gallons (average of 29,905 gallons per day)
- dedicated oil and gas treatment facilities: nearly 1 million gallons (average of 2,715 gallons per day).

The total volume of Marcellus-derived fluids generated in Pennsylvania and treated and disposed of in West Virginia facilities is 7.4 million gallons (average of 20,217 gallons per day) at one dedicated oil and gas treatment facility.

### **Evaporation**

The construction of storage impoundments or use of tanks where flowback water can, over time, evaporate into the air is a treatment option in the more arid West and Southwest, but this is not a viable option in the Mid-Atlantic, given our humid climate.

### **Where To from Here in Addressing the Challenges of Drilling Wastewater?**

Industry watchers expect the future breakdown of Marcellus wastewater treatment to look something like this (all percentages are approximate): brine disposal plants-35 percent; deep injection wells-10 percent; reuse/recycle-30 percent; advanced treatment (e.g., evaporators, crystallizers, membranes)-20 percent; publicly owned sewage treatment plants-10 percent.

### **New Well Casing Regulations**

Regulations strengthening oil and gas well construction standards to prevent methane gas migration became effective in February 2011. DEP's proposed regulations, which outline many standards that the industry must follow in drilling and casing new wells, were developed in response to recent incidents of methane gas migration into drinking water supplies, which pose public health and safety threats. The regulations also require drillers to detail the chemicals found in flowback water, and to electronically report production and waste volume data.

### **Conclusion**

The treatment, handling, disposal, reuse, and regulation of Marcellus wastewaters are very dynamic issues. Topics to watch for future developments include radioactivity in flowback water, out-of-basin and out-of-state flows, the potential for recycling frack water, and an improved system for tracking Marcellus water and wastewater flows, including reuse, transportation, treatment, and disposal.

In other U.S. shale gas fields, wastewater is often disposed of via underground injection or evaporation, neither of which works well in Pennsylvania, so the industry has had to come up with new solutions. Given the very high TDS levels in flowback water, traditional methods of wastewater treatment, such as reverse osmosis, don't work well. Another factor hindering innovation was the lack of a clear treatment target. Before DEP's new TDS regulation was finalized, the industry did not know how clean they would be required to get the wastewater, so they could not effectively choose a methodology to pursue. Adding to the confusion is the difficulty of obtaining sound data for things like the amount of flowback water being recycled or trucked out of state.

With DEP's recent finalization of the TDS and well casings regulations, a period of very rapid regulatory flux may be ending, clearing the way for innovation within the gas and water treatment industries. Questions remain about the capacity, methods, and costs required to meet the new effluent standards.

Citizens and other stakeholders are learning about the degree to which Pennsylvania DEP's policies, such as setting new water quality effluent standards, affect other states. With the substantial trucking of water and wastewater out of state and across river basin boundaries, hydrologic interconnections are being broken. Transportation may not be a sustainable long-term solution to wastewater

management. Also, there is no river basin commission in western Pennsylvania, where a good deal of the Marcellus drilling is occurring, so there may be a lack of consideration for the broader river basin picture. Water doesn't stop flowing at state boundaries. More interstate and possibly federal cooperation and coordination may be needed to ensure that gas exploration activities in states in the Marcellus region can meet the applicable standards to protect water resources.

*Please note that the information presented in this factsheet was current as of March 2011. The technologies and regulations are continually evolving. For more information see the following resources.*

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