



Is Reuse of Produced Water Safe?

First, Let's Find out What's in it

This articles considers the risks associated with reusing produced water from oil and gas production.

A proportion of produced water from conventional and unconventional oil and gas development is currently being reused to irrigate food crops, water livestock, recharge aquifers, create and maintain wetlands, and suppress dust, among other uses. Produced water is also sometimes treated at wastewater treatment plants (WWTPs) and discharged to surface water. As oil and gas field produced water is increasingly used, questions have arisen as to whether it is safe.

To answer this question, assessments of the chemical risks of reusing produced water must be undertaken and require the following: the identification and quantification of chemical compounds present in produced water (e.g., major ions, metals, organic compounds); sufficient information on the physiochemical (e.g., Henry's Law constants, solubility, vapor pressure, etc.) and biological (e.g., anaerobic and aerobic biodegradation, bioconcentration in humans, animals, and other biota) properties of compounds present in produced water; and adequate information on mammalian and ecological (e.g., aquatic) toxicity to estimate safe aqueous concentrations for protection of human health and the environment.

The fundamental question then is: do these conditions exist to properly evaluate risk posed by the reuse of produced water or discharge of partially treated produced water to land or water bodies?

Sources of Chemicals in Oil and Gas Produced Water

Chemical compounds present in produced water are sourced from four broad categories:

- **Chemical additives**, such as strong acids, corrosion inhibitors, biocides, scale inhibitors, iron control, and clay stabilizers used during routine oil and gas development operations (e.g., drilling and routine maintenance).^{1,2}
- **Additional additives**, such as gelling agents, foaming agents, crosslinkers, breakers, friction reducers, pH adjusters, and biocides used during well stimulation treatments (e.g., hydraulic fracturing and matrix acidizing).
- **Geogenic substances**, such as salts, heavy metals, radium, and hydrocarbons, brought to the surface during development.

The Need for Chemical Disclosure

Identification of the compounds in produced water logically begins with the requirements for disclosure of chemical additives used downhole during oil and gas development. Regulations in 21 of 27 oil and gas producing states now require the disclosure of chemicals used for hydraulic fracturing—

many through the voluntary FracFocus (<http://fracfocus.org/>) Chemical Disclosure Registry developed by the Ground Water Protection Council.³ It is unclear why disclosure for chemicals used during hydraulic fracturing is not required in all oil and gas producing states.

Disclosure, when required, is limited to chemicals that are not considered proprietary, which introduces significant uncertainty to risk assessment. Stringfellow et al.⁴ reviewed 1,623 hydraulic fracturing treatments entered into FracFocus for an estimated 5,000 – 7,000 hydraulic fracturing treatments known to have occurred in California between 2011 and 2014 (reporting rate ~23% – 32%) and found that 3,071 of 45,058 (~7%) of entries for additives were considered proprietary. Similarly, Shonkoff et al.² assessed chemicals used in steam injection oil fields in California that provide produced water to food crop irrigation and livestock watering and found that 46 percent of the compounds were reported as proprietary.

California appears to be the only state that requires disclosure of chemicals used for acid well stimulation treatments, including matrix acid stimulation and acid fracturing. There is considerable overlap in the chemicals used for routine maintenance acidizing (i.e., activities conducted in most oil and gas wells) and matrix acid stimulation,^{5,6} suggesting the need for expanded chemical disclosure for all acid treatments.

The South Coast Air Quality Management District in Southern California is the only regulatory agency in the United States that requires disclosure of chemicals used routinely during conventional oil and gas activities. There is extensive use of chemicals during routine oil and gas development operations (e.g., drilling, cementing, wellbore clean-outs, scale and corrosion control). The frequent overlap between chemicals used during hydraulic fracturing and these routine operations, as well as the observed larger number of chemicals used in these routine operations compared to those used in hydraulic fracturing,¹ suggests the need for chemical disclosure to be expanded to routine operations.

The Need for Chemical Analysis of Produced Water

While disclosure of chemicals used in routine operations and hydraulic fracturing and acidizing treatments is of considerable value in identifying compounds that could be present in produced water, actual chemical analysis of the waste stream prior to discharge of produced water is important from public health and environment perspectives. In some cases, produced water has been analyzed for inorganic composition (i.e., major ions, heavy metals, and radioactive elements) and to some extent for known organic additives. However, more

comprehensive analyses of organic compounds present in flowback and produced water is only in nascent stages.

The use of innovative analytical methods has resulted in the detection of organic compounds not routinely analyzed for or detected using standard U.S. Environmental Protection Agency (EPA) methods. Advanced methods for detection of organic compounds includes high-performance liquid chromatography with tandem mass spectrometry (HPLC–MS/MS),^{7,8} liquid chromatography quadrupole time-of-flight mass spectrometry (LC/Q-TOF-MS),⁹⁻¹² two-dimensional gas chromatography mass spectrometry (GCxGC-MS),¹³ GCxGC-MS coupled with time of flight analysis (GCxGC-TOF-MS), and ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS).¹⁴

The Need for Monitoring and Analysis of Chemical Transformation Products

Continued development of analytical methods is necessary to not only identify exotic organic compounds in produced water, but also to identify abiotic and biotic transformation products of these compounds. Strong oxidizers used during hydraulic fracturing may mediate abiotic reactions forming a variety of compounds in flowback and produced water, especially in saline water, such as halogenated benzenes, pyrans, alkanes, and acetones.¹³

For example, Leuk et al.¹⁴ detected numerous iodinated organic compounds in flowback samples (> 800 formulas in one

sample alone). The large numbers of iodinated compounds detected are of particular concern given the greater toxicity of iodinated disinfection byproducts compounds compared to their chlorinated and brominated counterparts.^{14,15}

Examples of biologically mediated transformation include the biocide 2,2-dibromo, 3-nitrilo propionamide used in nearly one quarter of hydraulic fracturing treatments, which biodegrades to dibromoacetone, a more toxic and persistent biocide.¹⁶ Alkoxylated nonylphenols, disclosed in around half of all hydraulic fracturing treatments, biodegrade to the relatively persistent endocrine disrupting compounds octylphenol and nonylphenol.¹⁶

The Need for More Complete Toxicological and Environmental Profile Information

There are also significant data gaps on physicochemical properties, biodegradability, and toxicity of a large number of compounds used in and associated with routine operations and hydraulic fracturing and acid stimulation.^{1,4,16-18}

For instance, in an attempt to assess the mobility, persistence, and toxicity of 659 organic compounds known to be used for hydraulic fracturing, Rogers et al.¹⁷ noted that experimental data on biodegradation existed for only 312 compounds (47%) of which only 47% (or 22% of the total number of compounds) were relevant for anaerobic conditions expected in subsurface media because of the high biological oxygen demand of additives.

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Yost et al.¹⁹ noted that chronic oral reference doses and cancer oral slope factors existed for only 83 and 23 of 1,076 compounds (or 8% and 2%, respectively) identified by EPA as used for hydraulic fracturing and 72 and 32 of 134 compounds (54% and 24%, respectively) detected in produced water. These findings along with other studies^{17,18} have identified gaps in toxicity information necessary to assess potential impact on public health.

The Need for More Information on Effectiveness of Treatment Prior to Reuse

Full identification of compounds in produced water and associated toxicity is necessary to evaluate the effectiveness of wastewater treatment facilities prior to discharge to surface water. For instance, Ferrer and Thurman⁹ detected the quaternary amine biocide alkyl dimethyl benzyl ammonium chloride (ADBAC) in flowback water. ADBAC is not effectively removed by conventional wastewater treatment and has been detected in surface water and sediment downstream wastewater sources.^{20,21}

Field studies on wastewater treatment of produced water in Pennsylvania indicate exceedance of maximum contaminant levels (MCLs) and incomplete removal of organic compounds^{22,23} prior to discharge to surface water. A large portion of compounds used in routine operations and in hydraulic fracturing and acid treatments are acutely toxic to aquatic life¹ necessitating estimation of safe aqueous concentrations prior to discharge to surface water.²⁴ In the San Joaquin Valley of

California, produced water used to irrigate food crops and water livestock is treated only by running it through a walnut shell filter with unknown effectiveness of removing chemicals of concern and associated transformation products.

Evidence of Impact

There are a number of recent studies indicating cause for concern with discharge or reuse of produced water. Warner et al.²⁵ detected elevated radium 226 (²²⁶Ra) and radium 228 (²²⁸Ra) having activities of 8,759 and 2,187 Bq/kg (both >2 orders of magnitude above background), respectively in sediment near the effluent of a WWTP in western Pennsylvania. These activities are higher than requirements for management of technologically enhanced naturally occurring radioactive material (TENORM; <http://www.tenorm.com/regs2.htm>), which range from 185 to 1,850 Bq/kg in the United States and require disposal in a licensed radioactive disposal facility. Radium is a known human bone, liver, and breast carcinogen²⁶ with bioaccumulation factors in freshwater fish, invertebrates, mollusks, and shells ranging from 100 to 1,000²⁵ and a half-life of 1,600 years.

Akob et al.²⁷ detected elevated ²²⁶Ra in sediment near a Class II disposal well receiving hydraulic fracturing wastewater in West Virginia in which produced water was previously stored in impoundments. Kassotis et al.²⁸ and Orem et al.²⁹ also investigated impact to this watershed with the former finding high levels of endocrine disrupting chemical activity in surface water extracts and the later finding numerous chemicals



In Next Month's Issue...

Environmental Management: A New Administration Takes the Reins

The Trump administration has set course on a new direction for U.S. policy on air and waste management. The September issue will provide an overview of new Administration priorities for the U.S. Environmental Protection Agency (EPA), as well as perspectives on those priorities from state, industry, and environmental groups.

associated with hydraulic fracturing in surface water and sediment.

Disinfection of water containing elevated levels of halides from upstream disposal of produced water can lead to the formation of trihalomethanes (THMs), haloacetonitriles (HANs), and halonitromethanes (HNMs). Hypochlorous acid/hypochlorite can oxidize bromide to hypobromous acid/hypobromite and react dissolved organic matter to form bromated THMs, HANs, and HNMs, which are more genotoxic and cytotoxic than their chlorinated counterparts.³⁰ Chloroamination can lead to the formation of iodinated

concentrations present in produced water can cause de facto chloramination during chlorination resulting in NDMA. Ammonium salts are widely used during hydraulic fracturing. Parker et al. (2014) also demonstrated that elevated levels of bromide and iodide during drinking water disinfections causes a shift in THM, HAN, and HNM formation toward brominated and iodinated analogues at wastewater volume fractions as low as 0.01%.

Conclusion

In conclusion, while a number of impacts of produced water reuse have been identified, organic compounds used in oil



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THMs, HANs, and HNMs, which are even more genotoxic and cytotoxic than brominated disinfection byproducts^{31,32} and are potentially tumorigenic.³³ Elevated bromide concentration during chloroamination promote the formation of the potent carcinogen N-nitrodimethylamine (NDMA).³⁴⁻³⁶

Hladik et al.³⁷ detected THMs, HANs, and HNMs, including dibromochloronitromethane (DBCNB), in surface water downstream of produced water discharge. HNMs as a class are mutagenic in Salmonella assays and potent genotoxins in mammalian cells.³² In laboratory studies, Parker et al.³⁸ demonstrated that elevated (>0.35 mg/L as N) ammonium

and gas development are not sufficiently disclosed, identified, and quantitated in produced water. As such, there are significant data gaps in information on the physicochemical and toxicological properties of compounds used downhole and likely present in produced water. Given this, it is clear that conditions do not currently exist to properly evaluate the risks posed by the reuse of produced water or discharge of partially treated produced water to surface water. Policies and research agendas should be promulgated that set a course to systematically assess the risks of produced water reuse to ensure that appropriate monitoring and treatment options exist prior to a further expansion of this practice. **em**

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