

# Potential Impact to Surface Water and Sediment from the Transport of Produced Water by Barge Along the Ohio River for Disposal in Class II Injection Wells

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## About PSE Healthy Energy

Physicians, Scientists, and Engineers (PSE) for Healthy Energy is a multidisciplinary, nonprofit research institute dedicated to supplying evidence-based scientific and technical information on the public health, environmental, and climate dimensions of energy production and use. We put our mission into practice by integrating scientific understanding across multiple disciplines, including engineering, environmental science, and public health. We conduct original research, translate existing research for nontechnical audiences, and disseminate scientific information and analyses to inform policy at the local, state, and federal levels. We focus on the overlap of energy production, public health, and the natural environment and produce vetted scientific analyses.

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## About the Authors

Dr. DiGiulio is a senior research scientist at Physicians, Scientists, and Engineers (PSE) for Healthy Energy and an affiliate at the Department of Civil, Environmental, and Architectural Engineering at the University of Colorado. Dr. DiGiulio completed a B.S. in environmental engineering at Temple University, a M.S. in environmental science at Drexel University, and a Ph.D. in soil, water, and environmental science at the University of Arizona. During his 31 years with the U.S. Environmental Protection Agency (USEPA), he conducted research on gas flow-based subsurface remediation (soil vacuum extraction, bioventing), groundwater sampling methodology, soil-gas sampling methodology, gas permeability testing, intrusion of subsurface vapors into indoor air (vapor intrusion), subsurface methane and carbon dioxide migration (stray gas), and solute transport of contaminants in soil and groundwater including that associated with hydraulic fracturing and pits used to dispose oil and gas waste. He assisted in development of EPA's original guidance on vapor intrusion and the EPA's Class VI Rule on geologic sequestration of carbon dioxide. While with the EPA, he routinely provided technical assistance to EPA regional offices and assisted in numerous enforcement actions. The focus of his current work is on understanding environmental impact from oil and gas development in the United States and abroad, especially in regard to surface and groundwater resources. He has served as an expert witness in litigation relevant to oil and gas development, has testified before State oil and gas commissions on proposed regulation, and has testified before Congress on the impact of oil and gas development on water resources.

Dr. Rossi completed a B.S. in Civil and Environmental Engineering from Penn State in 2009, and received his Ph.D. in Geology and Environmental Science at the University of Pittsburgh in 2016. His dissertation research focused on soil biogeochemistry and how land use and human activities affect hydrologic regimes, and by extension, major and trace metal dynamics. Following the completion of his dissertation, Dr. Rossi was a visiting scholar at the University of Pittsburgh, and devised a project to reconstruct the environmental legacy of industrial activities and coal-fired electricity generation in the Pittsburgh Metropolitan Area. Dr. Rossi held his first

postdoctoral appointment in 2017 at Temple University, where he examined the impact of land use and green infrastructure on surface and groundwater hydrology within the Philadelphia Metropolitan Area. In 2017 Dr. Rossi was awarded a NatureNet Science Fellowship with the Nature Conservancy and conducted postdoctoral research on oxygen dynamics in agricultural soils at Stanford University. Dr. Rossi's current work is on the impact of produced water from oil and gas activities on groundwater systems.

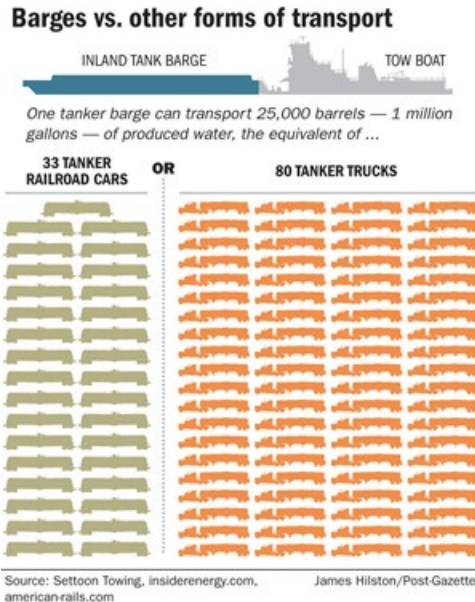
## Background

A network of river tank terminal and barge companies is in the process of securing permits to transport produced water (i.e., oil and gas wastewater) generated from unconventional oil and gas extraction in the Appalachian Basin on barges down the Allegheny, Monongahela, and Ohio Rivers. There are at least seven proposed river terminal sites spread out over hundreds of miles of the region's major waterways (Figure 1) (Hohey, 2021).

Interest in transporting produced water from the Marcellus and Utica Formations in Pennsylvania, Ohio, and West Virginia by barge on navigable rivers is being driven by anticipated cost savings compared to transporting produced water by tanker truck, railroad, and pipeline (Hohey, 2021). Produced water would be transported in double-hulled steel tank barges owned by Louisiana-based Settoon Towing, which has had U.S. Coast Guard (USCG) approval to barge oil and gas industry wastewater through Gulf Coast inland waterways for the last 30 years (Hohey, 2021). One tanker barge can hold approximately 25,000 barrels (1 million gallons) of produced water (Figure 2).



**Figure 1.** Proposed sites of river terminals for loading and unloading produced water by barge in the Allegheny, Monongahela, and Ohio Rivers. Figure source: Hohey, 2021.



**Figure 2.** Volume of produced water that one tanker barge can hold. Figure source: Hopey, 2021.

The proposed river terminals have potential implications for water quality near drinking water intakes. For example, the proposed tank and barge loading terminal along the Monongahela River in Speers, Washington County, 43.5 river miles above Pittsburgh’s Point (Hopey, 2021), is just one-half mile upriver from the Charleroi Municipal Authority’s water intake. Additionally, at least a half-dozen public and private water intakes are also downriver from the terminal. Among these intakes are three operated by the Pennsylvania American Water Co., which provide drinking water to approximately 583,000 people in Allegheny, Washington, and Fayette counties. The Nicholas terminal in Freeport, Armstrong County is located immediately upriver from the river water intake pipes of the Municipal Authority of Buffalo Township, which serves 8,000 people in Butler and Armstrong counties, including Freeport (Hopey, 2021).

According to a November 2019 USCG cargo authorization form, produced water will be offloaded to unloading terminals owned by Enlink Midstream at Bells Run near Portland, Ohio, and DeepRock Disposal Solutions, LLC, in Marietta, Ohio, located 160 and 173 river miles, respectively, from Pittsburgh (Hopey, 2021). Houston-headquartered DeepRock, a business partner with Comtech Industries, owner of the Bellaire terminal, operates twelve deep disposal wells at five sites near the unloading terminals in Ohio, and can accept up to 50,000 barrels or 2.1 million gallons of wastewater a day. A December 22, 2020 article on Comtech’s webpage states that DeepRock had received more than 30 permits and authorizations, is in “conversation” with river terminals on all three rivers, and was expected to begin receiving wastewater and unloading barges at its Marietta terminal during the first quarter of 2021 (Hopey, 2021). However, at this time, barging of produced water in Appalachia has not yet commenced.

In 2013, the USCG sent a proposal to the White House’s Office of Management and Budget to allow the barging of fracking wastewater (Gardner, 2013) into proposed barge locations in Meigs

County, Ohio and Ohio County, West Virginia (Hoopes, 2013). The USCG suggested a policy that limited load size and required characterization of each barge load of 30,000 barrels of hazardous waste on a case-by-case basis (Mauger, 2013). In this policy document, the USCG agreed to protect the industry's claim of "proprietary chemicals," but the chemicals had to be declared and each load characterized to identify its contents. This policy would have provided those who would be responsible for any spills and accidents with information on the material carried by each barge. In 2013, the proposed policy was put out for public comment (78 Fed. Reg., 2013). In 2016, after receiving over 70,000 public comments opposing the barging of produced waters on navigable Appalachian rivers, the USCG withdrew the proposed rule (81 Fed. Reg., 2016).

A USCG directive titled "Produced Water Classification" from July 2020 noted that the 2013 policy allowing the transport of shale gas extraction waste by barge, requested by the industry, was withdrawn that same year "primarily due to significant environmental concerns with transporting a potentially radioactive product" (Hopey, 2021). The document also states that because the chemical composition and radioactivity levels of the wastewater from different wells varies considerably, regular testing will be required (Hopey, 2021). Produced water carried on barges is considered a hazardous material by the USCG (Hopey, 2021) even though it is exempted as a hazardous material by the U.S. Environmental Protection Agency (USEPA) under Subtitle C of the Resource Conservation and Recovery Act. It is unclear who is responsible for accident management and spill mitigation—especially since the contents of each barge are not disclosed (Patterson, 2020).

The primary concern of transporting produced water by barges are spills, both periodic spills which are likely to occur, and catastrophic spills which could potentially occur. Spills may occur not only from barges but at loading and unloading facilities. Over the past decade in the Ohio River basin, which includes western Pennsylvania, Ohio, and West Virginia, extreme weather, especially high water, has been cited as a contributing cause in serious accidents (Kanik, 2020). Rising water levels during high water events obscures riverbanks and disturbs or transports river (alluvial) sediments, thereby changing the riverbed. Furthermore, these events can create currents that can pull vessels off course or throw debris into the path of a barge (Kanik, 2020). The U.S. Army Corps of Engineers estimates that up to 50% more water could be coursing through the Ohio River watershed within this century due to climate change (Drum et al., 2017). Kanik (2020) examined the USCG's database on inland accidents and found that serious accidents are on the rise. The USCG defines serious accidents as incidents involving death or serious injury, excessive property damage, or a discharge of hazardous materials. In 2010, about 8% of incidents were serious. By 2018, serious incidents accounted for 12% (Kanik, 2020).

The objective of this project is to elucidate potential contaminant pathways to human and ecological receptors from transporting produced water by barge on the Allegheny, Monongahela, and Ohio Rivers. Potential pathways for produced water to enter these rivers in this review include spills or a catastrophic release from barges and spills at loading and unloading facilities.

## Approach

In this report, our approach consists of reviewing available documents in the peer-reviewed literature, government reports, and grey literature on impacts to surface water and sediments resulting from produced water spills and discharges of produced water to surface waters. We searched the peer-reviewed literature with Google Scholar using combinations of search terms oil and gas development, produced water, hydraulic fracturing, and surface water.

We break our discussion into 4 parts: (1) the composition of produced water including transformation products generated during hydraulic fracturing; (2) the potential generation of disinfection byproducts during water treatment caused by produced water loadings; (3) case studies where impact to a stream located next to a Class II disposal well is documented; (4) case studies of radium buildup in sediment.

## Discussion

### 1. Composition of Produced Water in the Appalachian Basin

Produced water from unconventional oil and gas development has a complex chemistry that includes chemicals added for hydraulic fracturing and other production purposes (e.g., biocides, corrosion inhibitors, degreasers), transformation products of chemicals used for hydraulic fracturing and production, geogenic substances from the formation water (high dissolved ion content), and substances mobilized from the targeted formation (e.g., naturally occurring radioactive materials). Chemical characteristics of produced water of environmental concern include: organic compounds (Akob et al., 2015; Hladik et al., 2014; Orem et al., 2014; Thurman et al., 2014), toxic metals and metalloids (Lutz et al., 2013), radionuclides (Brown, 2014; Chapman et al., 2012; Rowan et al., 2011), and high salinity (Haluszczak et al., 2013; Rowan et al., 2011, 2015). Some of the identified chemical substances have potential health impacts, and include carcinogens such as polycyclic aromatic hydrocarbons, neurotoxins such as isopropanol, irritants such as sodium persulfate, and reproductive and endocrine toxins such as ethylene glycol and nonylphenols (Kassotis et al., 2014, 2015; Webb et al., 2014). Some of the organic substances present, such as glutaraldehyde, 2-butoxyethanol, 2,2-dibromo-3-nitrilopropionamide, and dibromoacetonitrile, may be toxic at low (ppb) concentrations. Environmental and human health impacts from unconventional oil and gas production may result if exposures occur from release of produced water due to spills during production activities, or improper handling, storage, transport, or disposal of produced water (Werner et al., 2015).

While produced water is commonly defined as the water returned by a well following a stabilization period, determined by a set amount of time following hydraulic fracturing, such as 14 days (Haluszczak et al., 2013), we use the term produced water to encompass any fluid returned by a well following hydraulic fracturing. Thus, the summary of produced water chemistry hereafter includes samples of both flowback and produced water.

## Lack of Full Disclosure of Chemicals Used for Hydraulic Fracturing

The identification of chemical constituents in produced water begins with requirements for disclosure of chemical additives used downhole during oil and gas development. The USEPA identified 692 unique ingredients reported for additives, base fluids, and proppants contained in more than 39,000 FracFocus disclosures (USEPA, 2015). In addition to these, compounds not typically associated with oil and gas development such as per- and polyfluoroalkyl substances (PFAS) are also utilized (Stringfellow et al., 2017a; Horwitt, 2021).

Regulations in 21 of 27 oil and gas producing states now require disclosure of non-proprietary chemicals used for hydraulic fracturing – many through the voluntary FracFocus Chemical Disclosure Registry developed by the Ground Water Protection Council (GWPC, 2014).

### *Disclosure requirements in Pennsylvania, Ohio, and West Virginia*

In Pennsylvania, well operators are required to complete a chemical disclosure registry form and post the form on the chemical disclosure registry (58 PA Cons Stat § 3222.1, 2016). However, operators are not required to disclose chemicals that they consider to be trade secrets or confidential proprietary information. Any health professional can request this information if it is needed to diagnose or treat a patient, but health professionals may be bound by the operator to a confidentiality agreement. Additionally, this code stipulates disclosures are not required for chemicals 1) that are not disclosed by the manufacturer, 2) not intentionally added to the stimulation fluid, and/or 3) those which occur in trace amounts, are the product of a chemical transformation, or are constituents of naturally occurring materials.

In Ohio, well operators are required to include the trade names, total amounts, and the purposes of all additives used during hydraulic fracturing in the well completion report (Ohio Rev. Code § 1509.10, 2021). This completion report is to be filed with the division of oil and gas natural resources management “within sixty days after the completion of drilling operations to the proposed total depth or after a determination that a well is a dry or lost hole.” Like Pennsylvania, operators in Ohio can withhold additive information that they deem to be a trade secret. However, unlike Pennsylvania, well owners are required to “make reasonable efforts to obtain the required information from the company or supplier.”

In West Virginia, well operators are required to submit a water management plan which includes a listing of anticipated additives that may be used for hydraulic fracturing (W. Va. Code § 22-6A-7, 2013). After well completion, operators must submit a list of the additives actually used during fracturing as part of the completion log.

The lack of disclosure requirements for proprietary chemicals introduces significant uncertainty to risk assessment, and insight into issues associated with disclosure can be gleaned from California. Stringfellow et al. (2017b) reviewed 1,623 hydraulic fracturing treatments entered into FracFocus out of an estimated 5,000 to 7,000 hydraulic fracturing treatments (a reporting rate of only ~23% to ~32%) known to have occurred in California between 2011 and 2014 and found that 3,071 of 45,058 (~7%) of entries for additives were considered proprietary. Similarly,



Shonkoff et al. (2016) 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% of the compounds were reported as proprietary.

There is considerable overlap between compounds used for hydraulic fracturing and routine production well activities (Stringfellow et al., 2017a). However, 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 for routine oil and gas well activities (e.g., drilling, cementing, wellbore clean-outs, maintenance, scale and corrosion control). Complete disclosure of chemicals used for well stimulation, acidizing, and routine well activities is critical to understanding pathways of exposure for these chemicals to reach human or ecological receptors. Such is the case for spills in and adjacent to the Ohio River.

### Generation of Transformation Products in Produced Water During Well Stimulation

Chemical additives used during well stimulation have the potential to undergo subsurface chemical transformations and return to the surface via produced water. Although degradation pathways and products have been established for some chemical additives under standard state conditions, downhole conditions including high temperatures and pressures common to well stimulation can result in altered biodegradation potentials and unexpected chemical reactions and degradation productions (Kahrilas et al., 2015). The formation of degradation byproducts from downhole chemical transformations is poorly understood, yet can have significant implications for produced water quality, treatment, and disposal, and for human health due to environmental releases (Abdullah et al., 2017).

Continued development of analytical methods is necessary to not only identify exotic organic compounds in produced water but to also 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 (Hoelzer et al., 2016). Examples of biologically mediated transformation include the biocide 2,2-dibromo, 3-nitrilo propionamide used in ~22% of hydraulic fracturing treatments which biodegrades to dibromoacetonitrile, a more toxic and persistent biocide (Elsner & Hoelzer, 2016). Alkoxyated nonylphenols, disclosed in ~50% of hydraulic fracturing treatments, biodegrade to the relatively persistent endocrine disrupting compounds octylphenol and nonylphenol (Elsner & Hoelzer, 2016). Luek et al. (2017) 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 compounds compared to their chlorinated and brominated counterparts (Richardson et al., 2008).

Current studies of degradation byproducts from chemical transformations related chemical usage in oil and gas development are limited to hydraulic fracturing (Hoelzer et al., 2016; Xiong et al.,

**Table 1.** Summary of studies investigating chemical transformations of specific chemical additives

related to hydraulic fracturing

| Study                   | Precursor chemicals  | Halides   | Halogenated categories                   | Detected products   | Conditions   |
|-------------------------|--|-----------|--|---|--|
| Sumner & Plata, 2018    | Epichlorohydrin, Cinnamaldehyde, DBNPA                                     | Cl, Br, I | alkanes, acetonitriles, alcohols, others | Chloroacetonitrile, dichloroacetonitrile, bromoacetonitrile, dibromoacetonitrile, tribromomethane, chloriodomethane, boromodichloromethane, dibromochloromethane, iodoacetonitrile, $\alpha$ -iodocinnamaldehyde, $\alpha$ -chlorocinnamaldehyde, $\alpha$ -bromocinnamaldehyde, 2,3-dichloro-1-propanol, 1,3-dichloro-2-propanol, 3-chloro-1,2-propanediol | Presence of oxidants (i.e., breakers) that can react with halides to form reactive intermediates, which then react with organic species. pH and temperature affect halogenated species formation rates and distribution. |
| Xiong et al. 2018, 2020 | Polyacrylamide   | -         | -  | Degraded short chain polyacrylamides<br>Possibility of acrylamide monomer formation   | Degradation caused by both physical shearing and chemical decomposition.   |
| Sumner & Plata, 2019    | Guar gum, Borate and zirconium crosslinkers, oxidant breakers, citric acid | Cl, Br, I | alkanes                                  | Bromochloromethane<br>Chloriodomethane<br>Bromodichloromethane<br>Dibromochloromethane<br>Chlorodiiodomethane<br>Bromodiiodomethane<br>Tribromomethane<br>Trichloromethane<br>Triiodomethane  | Halogenation requires high concentrations of oxidants. Citric acid more prone to trihalomethane formation than guar gum. Zirconium crosslinkers more prone to trihalomethane formation than borate based crosslinkers.   |
| Kahrilas et al., 2016   | Glutaraldehyde   | Br, Cl, I | -  | Glutaraldehyde dimers, trimers;<br>possibly unchanged depending on conditions   | Influenced by pH, temperature, and salinity. May readily degrade under hot, alkaline conditions. Likely to return to surface with transformation products in cooler, acidic, saline conditions.                          |

2018, 2020) (Table 1). The characterization of produced water in these studies has resulted in detection of compounds that cannot be attributed to geogenic sources or chemical additive sources (Hoelzer et al., 2016; Maguire-Boyle & Barron, 2014; Sumner & Plata, 2018). Hence, transformations of chemicals used during oil and gas development may have unknown consequences on public and environmental health, complicating risk assessment.

Halogenated organic compounds have been detected in multiple studies of hydraulic fracturing flowback and produced waters where they were not reported in chemical disclosures and are an area of growing concern (Evans et al., 2019; Hoelzer et al., 2016; Sumner & Plata, 2018). Halogenated benzenes, pyrans, alkanes, methanes, and acetones have been detected in hydraulic fracturing wastewaters from the Fayetteville Shale (Hoelzer et al., 2016) and chlorocarbons and

organobromides have been detected in produced water from the Barnett, Marcellus, and Eagle Ford formations (Maguire-Boyle & Barron, 2014). Evans et al. (2019) detected 20 organohalide compounds from Marcellus shale produced water including haloalkanes, haloamides, haloamines, halobenzenes, and haloesters. They determined microbial organohalide transformation may play a direct role in the formation of these organohalides, which are known to be relatively long-lived toxic contaminants (Krasner et al., 2006).

A study conducted by Sumner and Plata (2018) found that epichlorohydrin, cinnamaldehyde, and 2,2, dibromo-3-nitrilopropionamide (DBNPA) showed evidence of halogenation when subjected to simulated downhole hydraulic fracturing conditions. They concluded that halogenation reactions are facilitated by the following conditions.

1. Presence of oxidants (i.e., breakers) can react with halides to form reactive intermediates, which then react with organic species.
2. High concentrations of chloride, bromide, or iodide in formation waters increase the likelihood of halogenated product formation. Other factors including pH and temperature affect halogenated species formation rates and distribution.
3. Reaction kinetics are highly dependent on well temperature, increasing by an order of magnitude with a 40°C increase.

Another study by Sumner and Plata (2019) examined the downhole reaction of guar gum based fracturing fluids that use borate or zirconium crosslinkers with oxidative breakers. Under simulated conditions, oxidative breakers, such as persulfates, chlorites, and hypochlorites can react with other additives such as cinnamaldehyde and citric acid to form various halogenated transformation products.

Polyacrylamide is a common friction reducer used in slickwater hydraulic fracturing fluids in shale plays across the United States (Stringfellow et al., 2014). The degradation of polyacrylamide through both chemical and mechanical mechanisms in high volume hydraulic fracturing was investigated by Xiong et al. (2018, 2020). They found significant degradation in polyacrylamide due to both mechanical shearing and free radical chain scission mechanisms, resulting in a wide distribution in polyacrylamide molecular weights. The abundance of degraded polyacrylamide may complicate produced water treatment and increase the likelihood of acrylamide monomer release to the environment. Acrylamide is highly toxic and a likely human carcinogen. DBNPA is widely used as a biocide during hydraulic fracturing and may be a precursor to other halogenated organic compounds.

Glutaraldehyde is another commonly used biocide. A study of glutaraldehyde under simulated hydraulic fracturing conditions by Kahrilas et al. (2016) found that degradation of glutaraldehyde is influenced by pH, temperature, and salinity. Under downhole conditions, glutaraldehyde is suspected of undergoing autopolymerization, reactions with thiols and sulfides, or reactions with ammonia or amines. These transformation products could precipitate out of solution at high temperatures or under alkaline conditions, but would likely return to the surface with unreacted

glutaraldehyde products in cooler, more acidic, and saline conditions. The toxicity, and by extension, potential environmental impact of glutaraldehyde transformation products is unknown (Kahrilas et al., 2016).

Despite recent studies examining possible transformations of chemical additives, there remains a need to better characterize the potential transformation products and conditions that contribute to their formation (Kahrilas et al., 2016). Limited studies of widely used hydraulic fracturing chemical additives have shown there is a potential for multiple types of halogenated organic compounds to form and return to the surface with flowback and produced water. Other studies have detected similar compounds in produced water that do not match disclosed chemical additives or geogenic compounds. These halogenated organic compounds are generally environmentally persistent with varying degrees of human toxicity and are regulated in drinking water as disinfection byproducts. However, they are currently not regulated when they are constituents of produced water.

Furthermore, standard water quality monitoring methods and approaches overlook a variety of potential constituents found in produced water, including chemical additives and their transformation products. Using non-targeted analytical methods to monitor produced water quality, such as high-resolution mass spectrometry with liquid chromatography, is an emerging approach that could detect the presence of unknown or problematic transformation products, such as halogenated organic compounds. The potential impacts of discharges of produced water during barge transport (i.e., spills) on human and ecological receptors cannot be evaluated because the full suite of compounds in produced water cannot be identified and quantified. Thus, we know that there is a risk, but we cannot adequately evaluate or identify this risk.

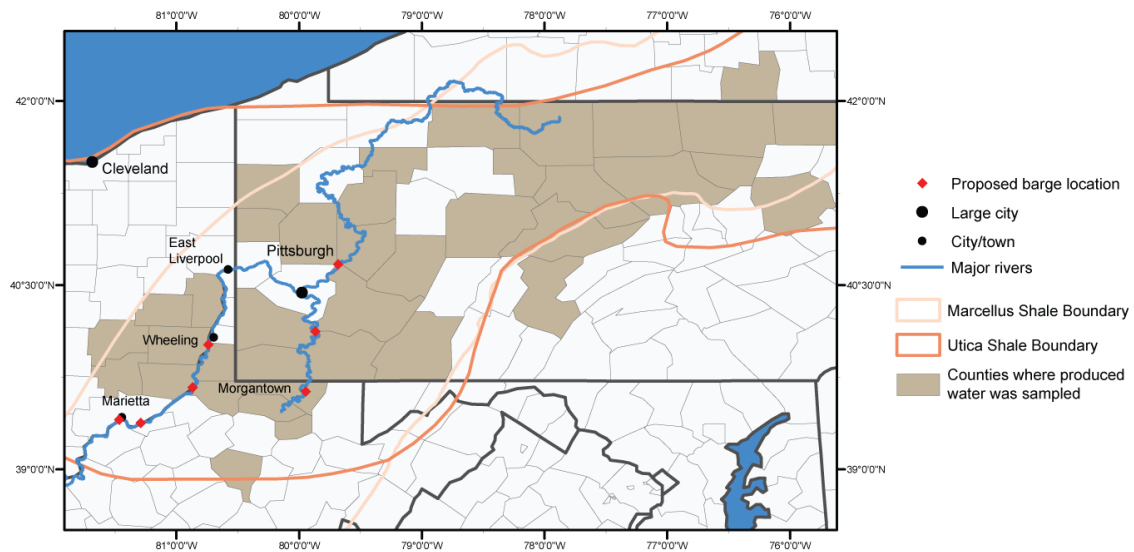
#### Summary of Chemical Composition of Produced Water in the Appalachian Basin

The disclosure of chemicals used in routine oil and gas development operations, hydraulic fracturing, and acidizing treatments is of considerable value in identifying compounds that could be present in produced water. However, a comprehensive analysis of produced water is necessary to understand potential risks to human health and ecological receptors that are posed by spills and other release mechanisms to surface water (e.g., wastewater treatment plant discharges, shallow groundwater flow). Since the onset of horizontal hydraulic fracturing operations in the Appalachian Basin in 2005 (Soeder & Kappel, 2009), samples of produced water have typically been analyzed for inorganic composition (major ions, heavy metals, and radioactive elements). However, organic additives have been measured at commercial laboratories relatively less commonly, and thus significantly less is known about occurrence and concentrations of these compounds.

These analyses have revealed that the chemical composition of produced water is extremely variable throughout the United States. Chemical analysis from commercial laboratories indicates that produced water can be saline (>10,000 mg/L TDS) to hypersaline (>100,000 mg/L TDS), have high concentrations of metals, contains volatile organic compounds including benzene, a

known human carcinogen and polycyclic aromatic hydrocarbons, and elevated levels of radionuclides such as radium which is also a known human carcinogen.

Here we provide a summary of 16 studies that have characterized Appalachian Basin produced water chemistry (Table 2). Concentrations of constituents are reported as ranges, to account for both the lack of information regarding laboratory detection limits in many of the datasets, and several of these studies using shared datasets. For example, data from Hayes (2009) was used by both Abualfaraj et al. (2014) and Haluszczak et al. (2013), in their respective analyses. However, Haluszczak et al. (2013) tabulated this data separately, whereas Abualfaraj et al. (2014) only provided aggregated summary statistics for all the data sources they considered. Reporting ranges of constituents accounts for this overlap and does not bias the data. As such, it is important to note that concentrations of constituents should not be assumed to be distributed uniformly across any provided range, and maximum and minimum bounds are given for general discussion.



**Figure 3.** Counties where produced waters were sampled in the literature synthesized for this report. Approximate locations of the proposed barging facilities (Hopey, 2021), the approximate extent of the Utica and Marcellus Shales (USEIA, 2016a, 2016b), and the Allegheny, Monongahela, and Ohio rivers (USGS, 2021b, 2021a, 2021c) are provided for location reference.

**Table 2.** Summary of data sources used to characterize Appalachian Basin produced water chemistry. Some data sources did not provide sampling location on a county basis, in those cases either the region of the state, or the state itself are provided.

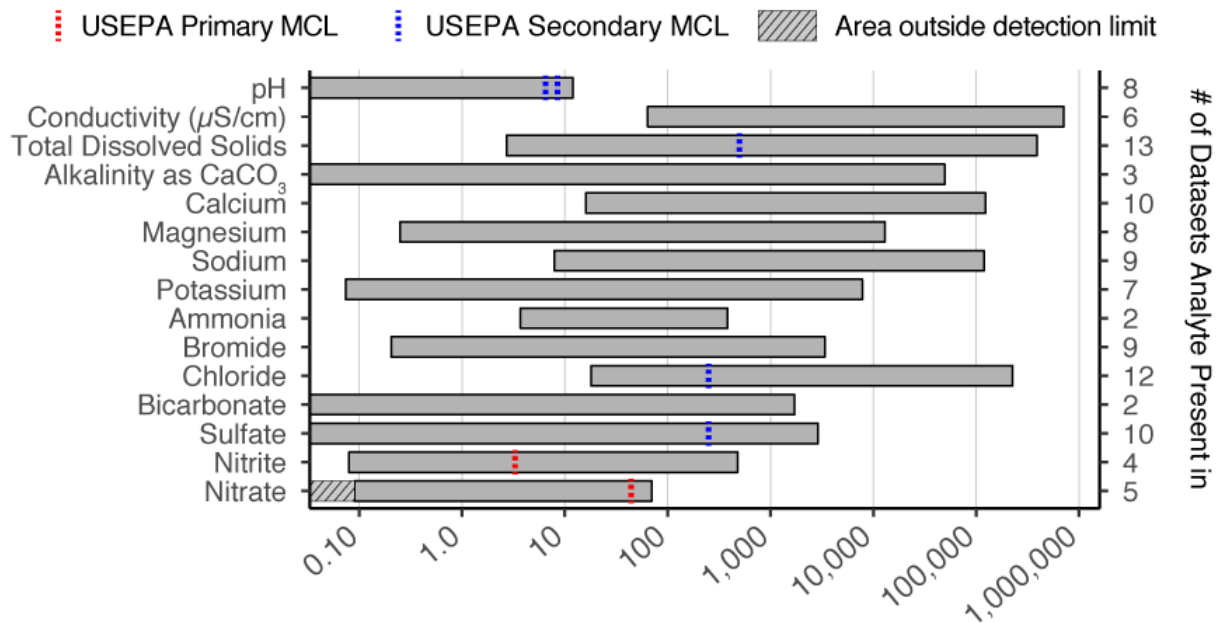
| Study                   | Formation | Sample Collection Area(s)  | Sample size             | Measured Constituents   |
|-------------------------|-----------|--|-------------------------|---|
| Blauch et al., 2009     | Marcellus | Southwestern PA; Northern WV   | 20                      | Barium; Calcium; Chloride; Electrical Conductivity; Hardness; Iron; Iron (II); Magnesium; Manganese; pH; Potassium; Sodium; Specific Gravity; Strontium; Sulfate; Total Dissolved Solids; Total Suspended Solids  |
| Hayes, 2009             | Marcellus | Bradford, PA; Butler, PA; Cameron, PA; Centre, PA; Greene, PA; Lycoming, PA; McKean, PA; Potter, PA; Washington, PA; Westmoreland, PA; Lewis, WV; Taylor, WV   | 86                      | Acidity; Amenable Cyanide; Ammonia Nitrogen; Biochemical Oxygen Demand; Bromide; Chemical Oxygen Demand; Chloride; Cyanide, Total; Dissolved Organic Carbon; Fluoride; Hardness as CaCO <sub>3</sub> ; Methylene Blue Active Substances; Nitrate as N; Nitrate-Nitrite; Nitrite as N; Oil & Grease; pH; Specific Conductance; Sulfate; Sulfite; Sulfite; Total Alkalinity; Total Dissolved Solids; Total Kjeldahl Nitrogen; Total Organic Carbon; Total Phosphorus; Total Recoverable Phenolics; Total Sulfide; Total Suspended Solids; Turbidity |
| Rowan et al., 2011      | Marcellus | Bradford, PA; Greene, PA   | 5 (TDS);<br>14 (Radium) | Radium-226; Radium-228; Radium, Total; Total Dissolved Solids   |
| Chapman et al., 2012    | Marcellus | Bradford, PA; Greene, PA; Washington, PA; Westmoreland, PA   | 35                      | Barium; Calcium; Chloride; Iron; Magnesium; Sodium  |
| Barbot et al., 2013     | Marcellus | Bradford, PA; Butler, PA; Cameron, PA; Centre, PA; Clearfield, PA; Clinton, PA; Fayette, PA; Greene, PA; Indiana, PA; Lycoming, PA; McKean, PA; Potter, PA; Susquehanna, PA; Tioga, PA; Washington, PA; Westmoreland, PA | NA <sup>a</sup>         | Alkalinity; Barium; Bromide; Calcium; Chemical Oxygen Demand; Chloride; Gross Alpha; Gross Beta; Iron; Magnesium; Oil and Grease; pH; Radium 226; Radium 228; Sodium; Strontium; Sulfate; Total Dissolved Solids; Total Organic Carbon; Total Suspended Solids; Uranium-235; Uranium-238  |
| Haluszczak et al., 2013 | Marcellus | Butler, PA; Cameron, PA; Clearfield, PA; Clinton, PA; Fayette, PA; Greene, PA; Huntingdon, PA; Indiana, PA; Somerset, PA; Susquehanna, PA; Washington, PA  | 22                      | Alkalinity as CaCO <sub>3</sub> ; Barium; Bromide; Calcium; Chloride; Electrical Conductivity; Manganese; pH; Potassium; Radium-226; Radium-228; Sodium; Strontium; Sulfate; Total Dissolved Solids; Uranium  |

|                         |           |  |                 |  |
|-------------------------|-----------|--|-----------------|--|
| Abualfaraj et al., 2014 | Marcellus | Bradford, PA; Butler, PA; Cameron, PA; Centre, PA; Clearfield, PA; Clinton, PA; Fayette, PA; Greene, PA; Indiana, PA; Lycoming, PA; McKean, PA; Potter, PA; Somerset, PA; Susquehanna, PA; Tioga, PA; Warren, PA; Washington, PA; Westmoreland, PA | NA <sup>a</sup> | 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; 1,2,4-Trichlorobenzene; 1,2-Dichloroethane; 1,2-Dichloropropane; Aluminum; Antimony; Arsenic; Barium; Benzene; Benzo(a)pyrene; Beryllium; Cadmium; Carbon Tetrachloride; Chlordane (Technical); Chloride; Chromium; Copper; Cyanide; Dibromochloromethane; Dinose; Endrin; Ethylbenzene; Fluoride; Gross Alpha; Heptachlor; Heptachlor Epoxide; Hexachlorobenzene; Hexachlorocyclopentadiene; Iron; Lead; Manganese; Mercury; Methoxychlor; Nitrate as N; Nitrite as N; Pentachlorophenol; pH; Radium-226; Radium-228; Selenium; Silver; Styrene; Sulfate; TDS; Thallium; Toluene; Toxaphene; Uranium-234; Uranium-235; Uranium-238; Vinyl chloride; Xylenes (total); Zinc   |
| Capo et al., 2014       | Marcellus | Greene, PA   | 58              | Calcium; Strontium   |
| Parker et al., 2014     | Marcellus | Western PA   | 2               | Ammonium as N; Bromide; Chloride; Dissolved Organic Carbon; Iodide; Nitrate as N; Nitrite as N; pH   |
| NYSDEC, 2015            | Marcellus | PA<br>WV   | NA <sup>a</sup> | Acetone; Acidity, Total; Alkalinity; Aluminum; Antimony; Aqueous ammonia; Arsenic; Barium; Benzene; Beryllium; Bicarbonates; Biochemical Oxygen Demand; Bis(2-ethylhexyl)phthalate; Boron; Bromide; Bromoform; Cadmium; Calcium; Cesium-137; Chemical Oxygen Demand; Chloride; Chlorodibromomethane; Chromium; Chromium (VI); Cobalt; Coliform, Total; Color; Copper; Cyanide; Dichlorobromomethane; Dissolved; Ethylbenzene; Fluid Density; Fluoride; Gross Alpha; Gross Beta; Hardness by Calculation; Heterotrophic plate count; Iron; Lead; Lithium; Magnesium; Manganese; Mercury; Methyl Bromide; Methyl Chloride; Molybdenum; Naphthalene; Nickel; Nitrate, as N; Nitrogen, Total as N; Oil and Grease; Petroleum hydrocarbons; pH; Phenol; Phenols; Phosphorus, as P; Potassium; Radium-226; Radium-228; Salt %; Scale Inhibitor; Selenium; Silver; Sodium; Specific Conductivity; Specific Gravity; Strontium; Sulfate (as SO <sub>4</sub> ); Sulfide (as S); Sulfite (as SO <sub>3</sub> ); Surfactants; Temperature; Tetrachloroethylene; Thallium; Titanium; Toluene; Total Alpha Radium; Total Dissolved Solids; Total Kjeldahl Nitrogen; Total Organic Carbon; Total Suspended Solids; Vanadium; Xylenes; Zinc |
| Phan et al., 2015       | Marcellus | Tioga, NY; Bradford, PA; Greene, PA; Washington, PA; Westmoreland, PA  | 43              | Manganese; Uranium   |

|                        |  |  |     |  |
|------------------------|--|--|-----|--|
| Rowan et al., 2015     | Marcellus; Burket; Bradford + Elk Groups | Greene, PA; Lycoming, PA; Tioga, PA  | 64  | Barium; Bicarbonate; Boron; Bromide; Calcium; Cesium; Chloride; Cobalt; Copper; Idoine; Iron; Lead; Lithium; Magnesium; Manganese; Nickel; Potassium; Rubidium; Sodium; Strontium; Sulfate; Total Dissolved Solids; Zinc   |
| Shih et al., 2015      | Marcellus                                | Armstrong, PA; Bradford, PA; Centre, PA; Clearfield, PA; Clinton, PA; Forest, PA; Greene, PA; Indiana, PA; Luzerne, PA; Lycoming, PA; McKean, PA; Potter, PA; Somerset, PA; Sullivan, PA; Susquehanna, PA; Tioga, PA; Washington, PA; Westmoreland, PA | 160 | Aluminum; Barium; Benzene; Calcium; Chromium; Copper; Electrical Conductivity; Gross Alpha; Gross Beta; Iron; Iron (II); Lithium; Magnesium; Manganese; Methylene Blue Active Substances; Molybdenum; Nickel; Oil and Grease; Potassium; Radium-226; Radium-228; Sodium; Strontium; Total Dissolved Solids; Uranium-234; Uranium-235; Uranium-238; Xylene; Zinc  |
| Ziemkiewicz & He, 2015 | Marcellus Utica                          | Marshall, WV; Marion, WV; Monongalia, WV; Wetzel, WV; OH; PA   | 13  | Alkalinity; Aluminum; Arsenic; Barium; Benzene; Bromide; Calcium; Chemical Oxygen Demand; Chloride; Chromium; Electrical Conductivity; Ethane; Ethylbenzene; Gross Alpha; Gross Beta; Hardness; Iron; Lead; Magnesium; Manganese; Mercury; Methane; Methylene Blue Active Substances; Nitrate; Nitrite; Oil & Grease; pH; Phosphate; Potassium; Potassium-40; Propane; Radium-226; Radium-228; Selenium; Silver; Sodium; Strontium; Styrene; Sulfate; Tetrachloroethene; Thorium-228; Thorium-230; Thorium-232; Toluene; Total Dissolved Solids; Total Organic Carbon; Total Suspended Solids; TPH (Diesel); TPH (Gas); TPH (Oil); Uranium-238; Xylene (m,p); Xylene (o); Zinc |
| Akyon et al., 2019     | Utica                                    | NA <sup>a</sup>  | 6   | Dissolved Organic Carbon; Total Dissolved Solids   |
| Tasker et al., 2020    | Utica                                    | Belmont, OH; Guernsey, OH; Harrison, OH; Jefferson, OH; Monroe, OH; Noble, OH; Mercer, PA; Lawrence, PA; Greene, PA; Potter, PA; Wetzel, WV  | 26  | Total Dissolved Solids; Chloride; Bromide; Sulfate; Lithium; Boron; Sodium; Potassium; Magnesium; Calcium; Strontium; Strontium-87/Strontium-86; Barium; Radium-226; Radium-228; Radium, Total; Iron; Copper; Arsenic; Cadmium; Lead; Uranium  |

<sup>a</sup> Source did not provide the total number of samples analyzed





**Figure 4.** Ranges of measured values of general chemical parameters and major ions as measured in Appalachian Basin produced waters. All analytes except pH and conductivity are in units of mg/L. The right y-axis indicates the number of datasets each analyte was measured in. Primary and secondary USEPA Maximum Contaminant Levels are provided for reference. Note, secondary standards indicate aesthetic issues, not human health issues.

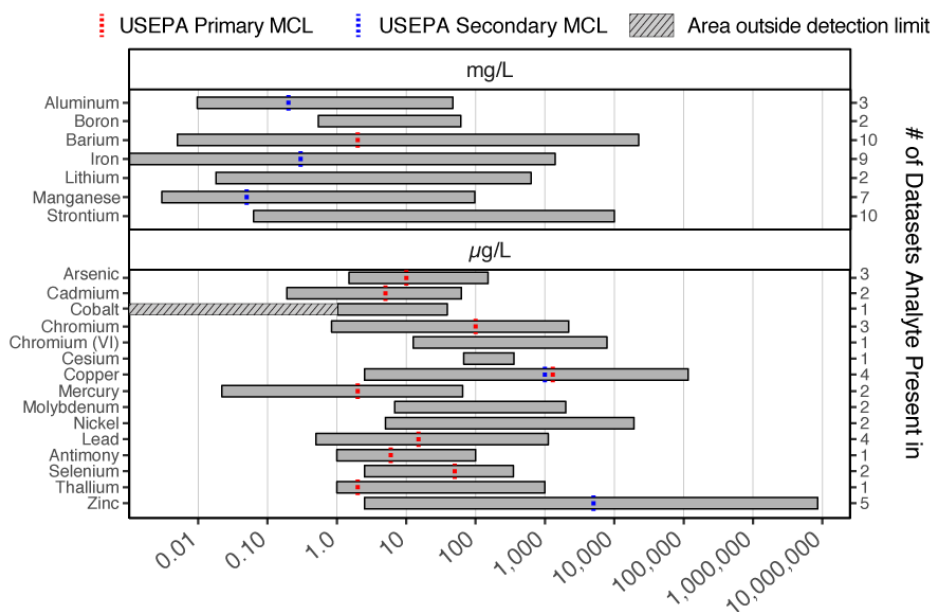
#### *Major ions and general chemical parameters*

Total dissolved solids (TDS) were the most commonly measured analyte in the compiled datasets. In general, chloride, sodium, and calcium dominate the TDS observed within Appalachian Basin produced waters (Barbot et al., 2013) (Figure 4). Concentrations of TDS generally increase as a function of time following hydraulic fracturing. For example, both Blauch et al. (2009) and Haluszczak et al. (2013) observed chloride concentrations to increase as a function of time following fracturing. In addition to temporal variation, concentrations of TDS in produced waters appear to vary on a regional basis, with Barbot et al. (2013) observing that calcium, magnesium, and chlorides concentrations in Northeastern Pennsylvanian produced waters were generally lower than those measured in Southwestern Pennsylvanian produced waters. Likewise, Marcellus Shale produced waters appear to have generally higher TDS concentrations (~3 – 390,000 mg/L) than Utica Shale produced waters (~71,000 – 288,000 mg/L) (Akyon et al., 2019; Tasker et al., 2020). Shih et al. (2015) observed the widest range in TDS concentrations (~3 – 390,000 mg/L), which serve as the lower and upper bounds of our compiled dataset.

The high concentrations of TDS in produced waters are of particular concern to riparian ecosystems, and drinking water intakes. Specifically, chloride can form relatively mobile complexes with heavy metals (e.g., cadmium, copper, lead) (Bäckström et al., 2004). Given the long history of industrialization in the Ohio River basin, alluvial sediments have received

substantial loadings of heavy metals (lead, zinc, cadmium) (Rossi et al., 2017). Significant loadings of chloride, due to accidental or chronic releases, could mobilize pools of legacy heavy metal contamination, transporting toxic metals to downstream receptors (e.g., drinking water intakes). Without numerical modeling, downstream transport distances of mobilized contamination are difficult to estimate. However, if an extensive barge transportation network were to be established, chronic releases of high TDS waters are likely, which could result in a relatively constant mobilization of sediment contamination and spread these harmful constituents downriver for miles.

In general, produced waters from the Appalachian Basin have relatively elevated concentrations of nitrogen species (ammonia, nitrite, nitrate) (Figure 4). In particular, the upper end of nitrate concentration ranges, and approximately half of nitrite concentration ranges exceed the associated USEPA primary MCLs (Figure 4). Additionally, the minimum and maximum measured ammonia concentrations in produced water are approximately 160 and 1,190 times higher than minimum and maximum ammonia concentrations, respectively, of Ohio River waters at East Liverpool (USGS, 2021). These elevated concentrations of nitrogen species are a particular concern for riverine ecosystems, as spills of produced waters have been documented to contribute substantial loadings of reactive nitrogen to surface waters (Cozzarelli et al., 2017). Nitrogen is a relatively common contaminant of surface waters, and excessive loadings to surface waters can lead to toxic algal blooms or fish kills (Carpenter et al., 1998).



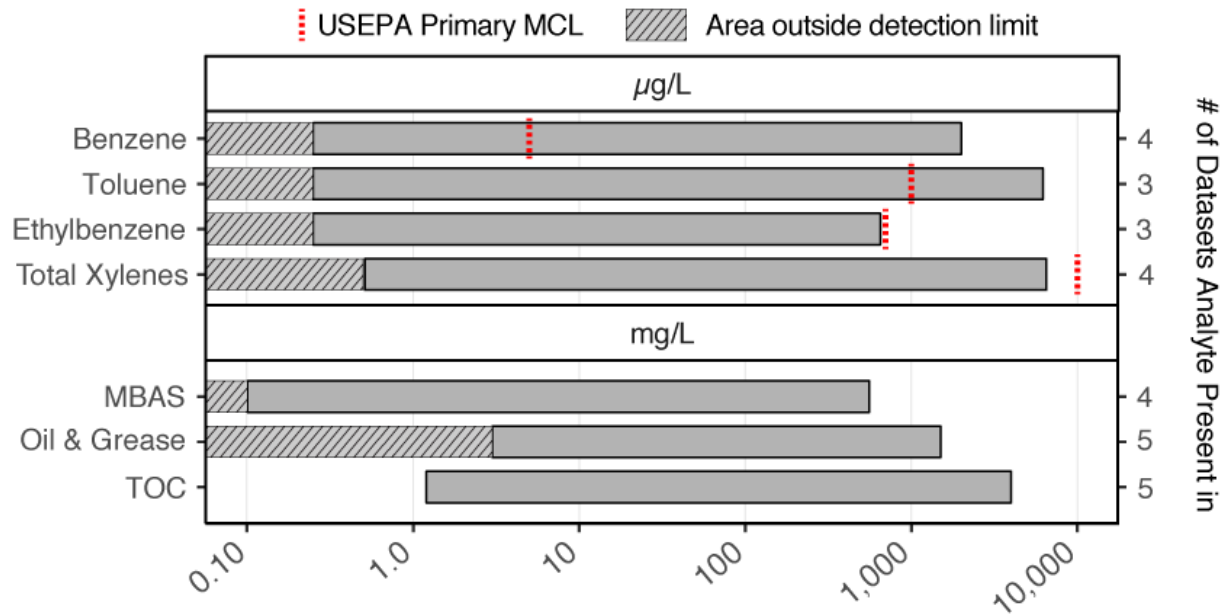
**Figure 5.** Ranges of measured values of trace elements, metals, and metalloids as measured in Appalachian Basin produced waters. The right y-axis indicates the number of datasets each analyte was measured in. Primary and secondary USEPA Maximum Contaminant Levels are provided for reference. Note, secondary standards indicate aesthetic issues, not human health issues.

### *Trace Elements, Metals, and Metalloids*

With the exception of barium, iron, and strontium, trace elements, metals, and metalloids are analyzed much less frequently than major elements and general chemical parameters (Figure 5). Barium concentrations measured in Appalachian produced water range from 0.005 to 22,400 mg/L, and more than half of this range is higher than the associated USEPA primary MCL (2 mg/L). Chapman et al. (2012) suggested that the barium in produced waters is sourced from the weathering of barium carbonate and barium sulfate minerals present in shales. Despite a relatively low number of epidemiological studies on barium exposure, cardiovascular failure and mortality were commonly observed in epidemiological studies that have examined the impact of chronic low-dose barium exposure (Kravchenko et al., 2014).

Concentrations of strontium in Appalachian produced water ranges from 0.063 to 10,300 mg/L. While strontium does not have an associated USEPA MCL, and likely poses no health impact at low levels (Zhang et al., 2018), strontium concentrations are particularly useful for forensic analyses. Specifically, multiple studies (Capo et al., 2014; Chapman et al., 2012; Tasker et al., 2020) have highlighted the utility of strontium isotopic ratios to fingerprint Appalachian Basin produced waters. While a powerful forensic tool, analyses of strontium stable isotopes are not as common as general chemical analyses. Tisherman & Bain (2019) suggest an alternative fingerprinting method, which uses calcium/strontium and calcium/magnesium (commonly measured water quality parameters) to identify Appalachian produced waters. Consequently, in the event of a major spill, strontium concentrations provide a method for scientifically determining how far and wide impacts of produced water spills may be.

Concentration ranges of trace metals with USEPA primary MCLs—arsenic, cadmium, chromium, copper, mercury, lead, antimony, selenium, and thallium—all exceed their associated MCLs (Figure 5). The maximum values of these constituents measured in produced water samples range from as low as 7 times the associated MCL (selenium) to as high as 500 times the associated MCL (thallium). While these metals are measured relatively less frequently than other chemical constituents (e.g., major ions) their presence in produced water represents a potential public and environmental health risk. For example, lead, the most commonly measured of these regulated metals, is a particularly notorious environmental contaminant and can cause neurological effects in children at particularly low doses (Needleman & Bellinger, 1991). Likewise, selenium, an endocrine disruptor (Vinceti et al., 2001), has been observed to bioaccumulate in aquatic food webs (Arnold et al., 2014), and thus even trace loadings may impair riparian ecosystems or affect humans who consume fish from these areas.

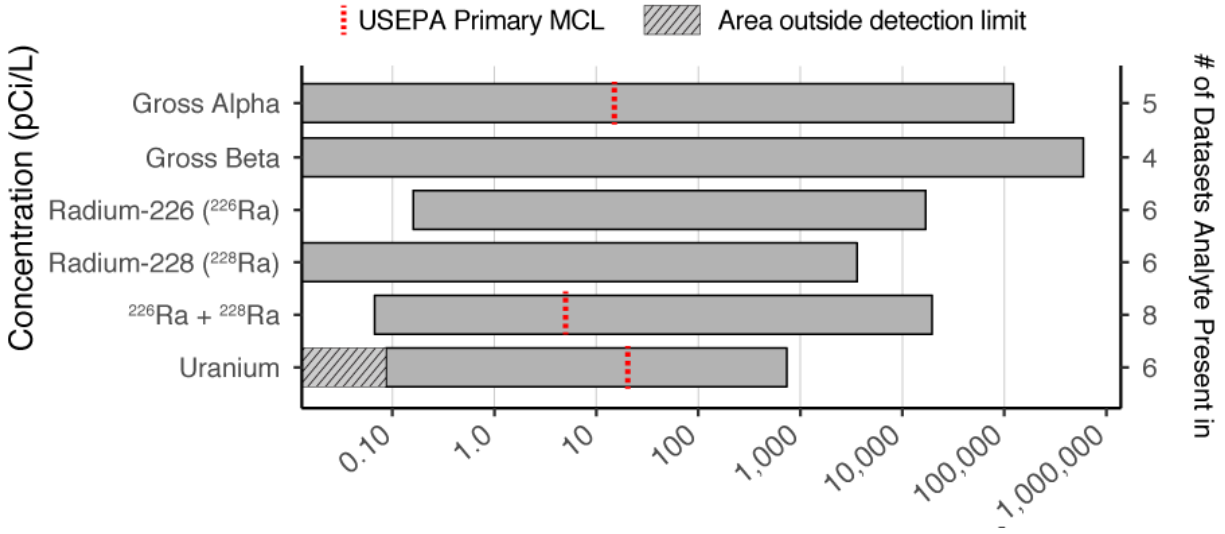


**Figure 6.** Ranges of measured values of organic compounds measured in Appalachian Basin produced waters. The right y-axis indicates the number of datasets each analyte was measured in. Primary USEPA Maximum Contaminant Levels are provided for reference.

### Organics

Organic compounds in Appalachian produced water are relatively under characterized as compared to other chemical constituents. Specifically, of the fifteen datasets examined only approximately a third of those reported concentrations of organic compounds. When organic compounds were reported, analytes were generally limited to BTEX compounds. Of the concentration ranges of BTEX compounds measured in produced water, the majority of measured benzene concentrations and the high end of measured toluene concentrations exceed the associated USEPA primary MCLs (Figure 6). Abualfaraj et al. (2014) had the most information regarding organic compounds, presumably taken from the USEPA dataset they analyzed. However, the majority of those compounds had few detectable concentrations. Thus, concentrations of organic compounds in produced waters are poorly characterized, and accidental releases of produced water may introduce these potential contaminants in unknown quantities to Ohio River waters.

Concentrations of Methylene Blue Active Substances (MBAS), a measure of surfactants, range from <0.10 to 240 mg/L. The oil and grease measured in produced water is likely a remainder following oil/water separation performed at the wellpad, indicating not all oil is removed during this treatment step. Concentrations of oil and grease range from <2.0 to 1,500 mg/L. Total organic carbon concentrations range from 1.2 to 3,990 mg/L, and presumably indicate residual hydrocarbons in produced water. Inputs of organic carbon from spill events, like TDS, have implications for legacy contamination pools in alluvial sediments. Inputs of organic carbon can



**Figure 7.** Ranges of measured values of radionuclides measured in Appalachian Basin produced waters. The right y-axis indicates the number of datasets each analyte was measured in. Primary USEPA Maximum Contaminant Levels are provided for reference.

possibly shift the oxidation-reduction potential of sediments, leading to the dissolution of iron-oxhydroxides which then may release bound toxic metal contaminants. Released contaminants may subsequently transported to downstream receptors (e.g., drinking water intakes, wildlife).

#### *Radionuclides*

Produced water from the Marcellus Shale is known to have high concentrations of radium (Figure 7). Abualfaraj et al. (2014) examined data sets from 92 wells associated with gas development in the Marcellus Shale, including that of Hayes (2009) and noted medium and maximum activities of radium-226 (<sup>226</sup>Ra) at 1,300 and 17,000 pCi/L (n=34), respectively and medium and maximum activities of radium-228 (<sup>228</sup>Ra) at 230 and 1,400 pCi/L (n=30), respectively in flowback water.

Nelson et al. (2014) found that matrix effects (i.e., high total dissolved solids concentrations) in produced water could decrease recovery of <sup>226</sup>Ra to just 1% of that present. Nelson et al. (2014) found that barium sulfate coprecipitation techniques followed by alpha particle spectroscopy (USEPA Method 903.0), radon emanation counting in a scintillation cell (USEPA Method 903.1), and beta particle spectroscopy (USEPA Method 904.0) can result in substantial underestimation of radium concentrations in solutions having high ionic strength. Nelson et al. (2014) recommended the use of direct high-purity germanium (HPGe) high resolution gamma spectroscopy for radium measurement in produced water samples. Thus, measurements of Ra in produced water using conventional methods could potentially significantly underestimate <sup>226</sup>Ra concentrations.

While measurements of radium concentrations in produced water using HPGe high resolution gamma spectroscopy are not subject to matrix effects, there are still uncertainties in radium measurements made using this method. For example, Tasker et al. (2019) compared radium

measurements of three produced water samples at 11 laboratories, most of which used gamma spectroscopy for measurement and noted that  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  measurements could be  $\pm 50\%$  and  $\pm 30\%$  of the most probable values calculated or median values. As a comparison, Eaton et al., estimated a  $\pm 20\%$  accuracy for  $^{226}\text{Ra}$  measurement in drinking water assessments. Hence, there is considerable uncertainty in the measurement of radium in produced waters.

Ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$  can be used to help identify the source of radium in surface water and sediment, but this source appropriation method relies on accurate concentration measurements. Ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$  range from 0 to 4 for all (i.e., conventional, and unconventional) produced waters from the Appalachian Basin (Rowan et al., 2011), with ratios of  $^{228}\text{Ra}/^{226}\text{Ra}$  for produced water from the Marcellus Shale being approximately 0.12 (Rowan et al., 2015). Radium from organic rich shales such as the Marcellus shale have low  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios because organic rich shales are enriched in uranium-238, the source of  $^{226}\text{Ra}$  compared to thorium-232, the source of  $^{228}\text{Ra}$ . Due to overlapping ranges in  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios of Ra-rich waters in the Appalachian Basin, inaccuracies in either  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  measurement reduce the effectiveness of source determination in the event of a spill. Thus increased Ra loadings could be falsely attributed to other potential Ra sources (e.g., conventional oil and gas brines, coal mine drainage).

#### Limits to Chemical Characterization of Produced Water

In its 2016 national report on hydraulic fracturing, the USEPA listed 1,606 chemicals that were reported to be used in hydraulic fracturing or detected in produced water of hydraulically fractured wells (USEPA, 2016b). Additionally, the USEPA identified 131 chemicals that had been detected in produced water but did not have an associated Chemical Abstract Service Registry Number (CASRN), a unique identifier to identify and differentiate between chemicals and synonymous chemical names. Importantly, the USEPA stated that, “standard analytical methods were not adequate for detecting and quantifying the numerous organic chemicals, both naturally occurring and anthropogenic, that are known to occur in produced water” (USEPA, 2016a). Produced water can contain total organic carbon (TOC) levels greater than 1,500 mg/L with only a minor portion of TOC characterized by standard USEPA methods (Rosenblum et al., 2017).

In its May 2018 report on Centralized Waste Treatment facilities, USEPA again stated that approved analytical methods do not exist for many constituents found in oil and gas extraction wastes (USEPA, 2018). The USEPA has stated further that some constituents (such as total dissolved solids) found in oil and gas extraction wastes can interfere with USEPA approved analytical methods and significantly affect the ability to detect and quantify the level of some analytes (USEPA, 2018). The identification and quantification of organic compounds in produced water can be challenging because of matrix effects (Nell & Helbling, 2019). The USEPA stated that there is a “primary data gap” in understanding the composition of produced water and produced water management (USEPA, 2018) which in this case includes transport by barge along the Ohio River.

Statements by the USEPA reflect the fact that a large number of compounds in produced water are unidentified. This is because while evolving research methods exist to identify a number of compounds present in produced water, these methods are not standard USEPA methods utilized at commercial laboratories. Also, even with advancements in analytical methodology, the ability to detect the complete suite of compounds in produced water is limited. Given the fact that new compounds are being continuously introduced into the market for oil and gas development makes the full identification of compounds present in produced water a nearly impossible objective. Nevertheless, chemical characterization using conventional methods provides insight into the chemical composition of produced water.

Comprehensive analyses and characterization of organic compounds present in flowback and produced water are 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 USEPA methods at commercial laboratories. Advanced methods for detection of organic compounds includes high performance liquid chromatography with tandem mass spectrometry (HPLC–MS/MS) (DeArmond & DiGoregorio, 2013b, 2013a), liquid chromatography quadrupole time-of-flight mass spectrometry (LC/Q-TOF-MS) (Ferrer & Thurman, 2015; Lester et al., 2015; Thurman et al., 2014, 2017), two-dimensional gas chromatography mass spectrometry (GCxGC-MS) (Hoelzer et al., 2016), GCxGC-MS coupled with time of flight analysis (GCxGC-TOF-MS), and ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) (Luek et al., 2017). For instance, Ferrer and Thurman (2015) detected the quaternary amine biocide alkyl dimethyl benzyl ammonium chloride (ADBAC) in 54% of samples collected from flowback water in Weld County, CO. ADBAC is not routinely analyzed at commercial laboratories and is not effectively removed by conventional wastewater treatment. Therefore, ADBAC could be present in drinking water sources downstream from where produced water is discharged (either intentionally or unintentionally).

#### Lack of Information on Physicochemical and Biological Properties of Compounds Associated with Produced Water Limits Fate and Transport Studies

There are data gaps on physicochemical properties (e.g., Henry's Law Constants for volatility, soil-water or octanol-water partition coefficient to evaluate sorption to solids) and biological properties (e.g., aerobic and anaerobic biodegradability) of a large number of compounds used in, and associated with, routine operations and hydraulic fracturing and acid stimulation (Elsner & Hoelzer, 2016; Rogers et al., 2015; Stringfellow et al., 2017a; Stringfellow et al., 2017b; Stringfellow et al., 2014). In an attempt to assess the mobility, persistence, and toxicity of 659 organic compounds known to be used in hydraulic fracturing, Rogers et al. (2015) noted that experimental data on biodegradation existed for only 312 compounds (47%) of which only 22% of these 659 compounds were relevant for anaerobic conditions.

In the absence of adequate information on the physicochemical and biological properties of compounds associated with produced water, it is not possible to discern the fate and associated risk of many compounds discharged or spilled into surface water. Thus, this knowledge gap

precludes assessing the totality of impacts to nearby receptors that would result from spills associated with barging operations, making the barge loading, transport and unloading of produced water on a major drinking water source problematic. In short, the absence of knowledge does not indicate the absence of harm, and government agencies and industry cannot scientifically posit that produced water is completely safe.

#### Lack of Information on Toxicological Impacts Limits Risk Assessments

The toxicological properties of a compound in produced water can only be evaluated if the compound has been disclosed with an associated CASRN. In an assessment of chemical additives used in hydraulic fracturing and matrix acid stimulations in California, Shonkoff et al. (2015) identified 320 chemical additives, 127 (40%) of which lacked CASRNs and/or lacked available toxicity information. In an assessment of chemical additives used in routine oil and gas development in the California South Coast Air Quality Management District, (Stringfellow et al., 2017b) identified 525 chemical additives, 233 (44%) of which lacked CASRN and an additional 140 (27%) that lacked available toxicity data. Hence, the toxicity associated with a large spill would be difficult to evaluate.

Shonkoff et al. (2016) evaluated toxicological properties of chemical additives disclosed between January 2014 and June 2016 used in oilfields that reuse produced water for agricultural irrigation and groundwater recharge in the San Joaquin Valley, CA. Shonkoff et al. (2016) found that of 173 chemical additives disclosed, 66 (38%) were classified as a “trade secret” or did not have a valid CASRN. Of the remaining identifiable chemicals, 13% (14 compounds) lacked any acute ecotoxicity or mammalian toxicity data and could not be evaluated.

In a more recent draft toxicological assessment by GSI Environmental (2020) for the California Central Valley Regional Water Quality Control Board, 385 chemical additives were disclosed as used in oilfields in which produced water was reused for agricultural irrigation in the San Joaquin Valley. Of these compounds, 73 (19%) could not be definitively identified or lacked toxicity information and 173 (45%) were assigned toxicity values derived by the consultants or toxicity values extrapolated from the published literature. The accuracy of these extrapolated values is unknown. The remaining 139 compounds (36%) were evaluated for toxicity using authoritative lists and databases. Thus, there is considerable uncertainty in the toxicological assessment for the majority of these compounds.

In a national assessment of chemical usage in hydraulic fracturing activities, Yost et al. (2016) noted that chronic oral reference doses existed for only 83 of 1,076 (~8%) of compounds identified by USEPA as used for hydraulic fracturing. Cancer oral slope factors existed for only 23 of these compounds. Yost et al. (2016) also noted that chronic oral reference doses existed for only 72 of 134 (~54%) of compounds detected in produced water from hydraulically fractured wells. Cancer oral slope factors existed for only 32 of these compounds. These findings along with other studies (Rogers et al., 2015; Stringfellow et al., 2014) have identified gaps in toxicity information necessary to assess potential impact on public health. Therefore, toxicity associated



with produced water continues to be largely unknown.

As previously discussed, chemical disclosure, while a helpful step in toxicological evaluation of produced water constituents, does not account for chemical transformations that may occur as produced water and its associated constituents undergo changes in temperature, pressure, and pH. In certain cases, chemical transformations may result in more toxic or more environmentally persistent byproducts (Kahrilas et al., 2015). Also, chemical usage in oil and gas operations is evolving over time and can vary between operators, activity, geologic formation, and field area.

Many chemical additives used and observed in produced water not only lack toxicological information, but as previously discussed, also lack standardized methods necessary for detection using targeted analytical approaches. However, in the event of a major spill, various non-targeted and bioanalytical methods may be appropriate to evaluate toxic potential of produced water, particularly in cases where exposure pathways are more likely (e.g., produced water discharged to the surface or reused outside the oilfield).

Bioanalytical approaches (e.g., cell line assays) can also be employed to supplement water quality testing to assess the toxicity of flowback and produced water (He et al., 2017; Liberatore et al., 2017; Tasker et al., 2018; Yao et al., 2015) and synthetic mixtures of constituents detected in flowback and produced water (Kassotis et al., 2015, 2018; Kassotis, Tillitt, et al., 2016; Robert et al., 2018). Experimental findings in the peer-reviewed literature demonstrate adverse effects to the endocrine, metabolic, and reproductive systems associated with the known and unknown substances that comprise produced water (He et al., 2017; Kassotis, Bromfield, et al., 2016; Kassotis et al., 2018; Kassotis, Iwanowicz, et al., 2016; Tasker et al., 2018). Hence, even in the absence of detected compounds, produced water can exhibit toxicity. Thus, spills of produced water via barging operations introduces poorly constrained risks to both communities relying on Ohio River waters for drinking water and nearby ecosystems.

## **2. Produced Water Discharge or Spills Can Result in Generation of Disinfection Byproducts During Water Treatment**

The high concentrations of halides (e.g., chloride, bromide) in produced waters can lead to the generation of disinfection byproducts (DBPs) at drinking water intakes downstream of produced water discharges. In the absence of desalination or use of membrane technology, halides pass through a treatment system unaffected. Disinfection of water containing elevated levels of halides from upstream disposal of produced water can lead to the formation of trihalomethanes (THMs), haloacetonitiles (HANs), and halonitromethanes (HNMs). Hypochlorous acid/hypochlorite can oxidize bromide to hypobromous acid/hypobromite and react with dissolved organic matter to form bromated THMs, HANs, and HNMs which are more genotoxic and cytotoxic than their chlorinated counterparts (Richardson et al., 2007). Chloroamination can lead to the formation of iodinated THMs, HANs, and HNMs which are even more genotoxic and cytotoxic than brominated disinfection byproducts (Plewa et al., 2004; Richardson et al., 2008) and are potentially tumorigenic (Wei et al., 2013). Elevated bromide concentration during

chloroamination promotes the formation of the potent carcinogen N-nitrodimethylamine (NDMA) (Luh & Mariñas, 2012; Shah et al., 2012; Shah & Mitch, 2012).

Hladik et al. (2014) 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 genotoxicants in mammalian cells (Plewa et al., 2004). In laboratory studies, Parker et al. (2014) demonstrated that elevated (>0.35 mg/L as N) ammonium concentrations present in produced water can cause *de facto* chloramination during chlorination resulting in NDMA. Ammonium salts are widely used during hydraulic fracturing, and consequently, the ammonium concentrations measured by Parker et al. (2014) (~67 mg/L as N), which far exceed this threshold, are likely not unique to that study. Parker et al. (2014) also demonstrated that elevated levels of bromide and iodide during drinking water disinfectants causes a shift in THM, HAN, and HNM formation toward brominated and iodinated analogues at wastewater volume fractions as low as 0.01%.

Drinking water treatment plants downstream of CWT facilities treating oil and gas extraction wastewater have noted a shift in the composition of DBPs from mostly chlorinated DBPs to brominated DBPs (USEPA, 2018). Multiple drinking water intakes are situated downstream of CWTs accepting oil and gas extraction wastewater within distances at which impacts to drinking water from CWTs have been identified (USEPA, 2018). This is especially true in the Ohio River Basin, as in 2008 DBPs were detected in drinking water plants intaking Monongahela River waters (Wilson & Van Briesen, 2013), and in 2011 the Pittsburgh Water and Sewer Authority (who has water intakes on the Allegheny River) were measuring levels of THMs that were near drinking water standards (Hopey, 2011). Wilson and Van Briesen (2013) concluded that discharges of shale gas wastewaters from CWTs were likely responsible for the increased bromide loadings.

While discharges of shale gas wastewaters from CWTs in Western Pennsylvania have decreased since 2011 (Hladik et al., 2014), DBP issues continue to affect drinking water resources in the Pittsburgh Metropolitan area (Marusic, 2019). Increasing discharge opportunities will increase the potential for ingestion and inhalation (through showering, laundry use, etc.) of toxicants and carcinogens from disinfected drinking water.

### **3. Case Studies of Impact to a Stream Located Next to a Class II Disposal Well**

The U.S. Geological Survey (USGS) collected surface water and sediment samples from an unnamed tributary which drains into Wolf Creek near Lochgelly in central West Virginia to evaluate impact as a result of disposal of produced water into a Class II disposal well facility located adjacent to the unnamed tributary. Wolf Creek discharges into the New River which is a drinking water source for the city of Fayetteville, WV (Akob et al., 2016; Orem et al., 2017). The study was part of a broader effort by the USGS Toxic Substances Hydrology Program to investigate the environmental and human health impacts of unconventional oil and gas wastes (Orem et al., 2017). This study is informative in understanding risks posed by the injection of

produced water into a Class II UIC disposal well adjacent to the Ohio River.

A description of the facility is provided by Akob et al. (2016) and Orem et al. (2017). A disposal well was originally drilled in 1981 as a natural gas production well to a depth of 990.6 m. The well was reworked as a Class II injection well in 2002, with fluids injected into a sandstone reservoir at a depth of 792.5 m. In addition to the disposal well, the facility has brine storage tanks, an access road, and two small, lined impoundment ponds. As originally configured, produced water transported to the facility in tanker trucks was transferred to impoundment ponds to allow for settling of particulates prior to injection. The ponds operated from 2002 to spring 2014 when they were removed and the area recontoured and planted with grass. Potential pathways considered for produced water to enter surface water or groundwater included: direct, accidental release from tanker trucks at the site, leakage from onsite storage ponds or tanks, migration of wastewater through subsurface aquifers at the injection depth or through failed casing in the UIC well, and runoff of contaminants spilled on the well pad in rainwater or snow melt (Akob et al., 2016; Orem et al., 2017).

Akob et al. (2016) observed elevated levels of electrical conductivity, chloride, bromide, strontium, and non-volatile dissolved organic carbon (NVDOC) adjacent to and downstream of the facility compared to upstream values. Upstream values of electrical conductivity, chloride, bromide, strontium, and NVDOC were 80  $\mu\text{S}/\text{cm}$ , 0.88 mg/L, <0.03 mg/L, 53.6  $\mu\text{g}/\text{L}$ , and 1.13 mg/L, respectively while downstream values were as high as 416  $\mu\text{S}/\text{cm}$ , 119 mg/L, 0.80 mg/L, 830  $\mu\text{g}/\text{L}$ , and 3.48 mg/L, respectively. Examination of strontium isotopic ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) in surface water samples corroborated evidence of impact to surface water in addition to observation of elevated  $^{226}\text{Ra}$  in sediment (2.8 pCi/g downstream compared to 0.71 pCi/g upstream) and radium-226/uranium-238 ( $^{226}\text{Ra}/^{238}\text{U}$ ) activity ratios in sediment in excess of unity (2.6) indicating lack of secular equilibrium (equivalent activities of  $^{226}\text{Ra}$  and  $^{238}\text{U}$ ) indicating potential enrichment of  $^{226}\text{Ra}$  from an external source beyond that naturally occurring in sediment.

Orem et al. (2017) analyzed surface water and sediment samples for organic compounds using gas chromatography (GC) and an electron ionization mass spectrometry (MS) detector operated in scan mode. Many peaks in the GC/MS chromatograms could not be identified using mass spectral libraries with sufficient accuracy (mass spectral matches not specified) and were not reported. Hence, many compounds in surface water and sediments associated with produced water could not be identified.

Orem et al. (2017) also conducted human cell line toxicity testing using liver and kidney cell lines. These cell lines represent two major systems used in the human body for metabolism of toxic substances. Acute 24-hour toxicity testing and clonal efficiency (CE) screening were performed using human liver cells. The CE screening measures the potential of the sample to promote cell growth. Anchorage independent growth (AIG) studies were performed on kidney cells.

Orem et al. (2017) found two locations downstream from the disposal facility that contained organic compounds in water that were consistent with a source from unconventional produced water. These compounds included: 2-(2-butoxyethoxy)-ethanol, tris(1-chloro-2-propyl)phosphate,  $\alpha$ ,  $\alpha$ -dimethyl-benzenemethanol, 3-ethyl-4-methyl-1H-pyrrole-2,5-dione, and tetrahydro-thiophene-1,1-dioxide in water, diesel fuel hydrocarbons (e.g. pentacosane, Z-14-nonacosane), and halogenated hydrocarbons (e.g., 1-iodo-octadecane, octatriacontyl trifluoroacetate, dotriacontyl pentafluoropropionate) in sediments. Biocides were not detected. Many biocides are not stable in unstable and biodegradable (Kahrilas et al., 2015). Concentrations of organic compounds in surface water derived from produced water varied from <1 to 4  $\mu\text{g/L}$ . Of particular interest was an unresolved complex mixture (UCM) at one downstream location indicating a mixture of hydrocarbons present in such abundance that the GC column was unable to resolve individual compounds resulting in a “hump” in the chromatogram.

Organic compounds associated with unconventional oil and gas development were detected in sediment at concentrations from 2.0 to 63 mg/kg (dry weight). At locations upstream from the facility or in nearby watersheds not influenced by the disposal well facility organic compounds detected in sediment were of natural (biologically produced) origin. Interestingly, at one location immediately downstream of the facility, numerous halogenated (fluorinated, chlorinated, brominated, and iodinated) hydrocarbons that are not disinfection byproducts were detected. Some of these compounds have been observed in wastewater from shale gas wells (e.g., dotriacontyl trifluoroacetate, 1,54-dibromotetrapentacontane) while others are of unknown origin (Orem et al., 2017).

Impact to surface water at this facility was further corroborated by (Kassotis, Iwanowicz, et al., 2016) who reported high levels of endocrine disruption chemical (EDC) activity in samples collected adjacent and downstream of the facility relative to samples collected at an upstream location. EDCs are exogenous mixtures of chemicals that can interfere with any aspect of hormone action (Zoeller et al., 2012). It has been demonstrated that chemicals used for unconventional oil and gas production includes EDCs (Kassotis et al., 2014, 2015; Kassotis, Tillitt, et al., 2016; Webb et al., 2014). Bioassay testing such as EDC testing is critical in evaluating toxicological endpoints given the inability to fully characterize the chemical composition and chemical-specific toxicological profile of produced water. A shift in microbial community structure, potentially affecting nutrient cycling, in sediment samples adjacent and downstream of the facility compared to an upstream sediment sample was also observed (Fahrenfeld et al., 2017). Thus, the findings of Akob et al. (2016) indicate an impact to surface water and sediment due to activities at the facility, although the pathway of contamination (e.g., out-of-zone migration from the Class II well, spills or leakage from impoundments) could not be discerned.

#### **4. Case Studies of Radium Buildup in Sediment**

Of considerable concern is the buildup of radium deposited in sediment downstream of a spill

location. Produced water from the Marcellus Shale is exceptionally radiogenic with radium isotope concentrations generally varying between 185 to 592 Bq/L (Rowan et al., 2011), although radium concentrations from conventional oil and gas development in the Appalachian Basin is also high with total radium activities up to 250 Bq/L (Rowan et al., 2011).

Radium is a known human carcinogen associated with cancers of the breast, blood, bone, and liver (ATSDR, 1990) with bioaccumulation factors in freshwater fish, invertebrates, mollusks, and shells ranging from 100–1,000 (Warner et al., 2013). (Ramirez, 2002) found that bone tissue from birds inhabiting a wetland receiving produced water near Cody, Wyoming contained  $^{226}\text{Ra}$  in addition to metabolites of polyaromatic hydrocarbons in bile.

Most of what is known regarding the disposition of radium in sediment comes from studies of discharge of untreated or partially treated produced water to surface water. The drinking water standard for  $^{226}\text{Ra} + ^{228}\text{Ra}$  is 0.185 Bq/L (5 pCi/L). Once discharged to surface water, the concentration of dissolved radium decreases due to association with settling particles and precipitating ions with subsequent accumulation in streambed sediments. Radium in sediment can be adsorbed to clay minerals, organic matter, or ferric and manganese oxides or coprecipitated with barium sulfate, strontium sulfate, or calcium carbonate minerals (Carvalho et al., 2014). Radium adsorption increases with decreasing salinity (Krishnaswami et al., 1991; Sturchio et al., 2001; Webster et al., 1995). The mixing of the saline wastewater with upstream low-saline water enhances Ra adsorption onto the sediments (Warner et al., 2013). However, radium can be released to a degree under sulfate reducing conditions (Ouyang et al., 2017; Phillips et al., 2001; Renock et al., 2016). Carbonates containing radium can dissolve in response to acidification (McDevitt et al., 2019). The half-lives of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are 1,600 and 5.76 years, respectively.

Bioaccumulation of Ra is known to occur in freshwater fish, invertebrates, mollusks, and shells with reported concentration factors (CF) of 100–1,000 (Hameed et al., 1997; Iyengar & Rao, 1990; Sturchio et al., 2001). Radium also accumulates in freshwater plants with an apparent CF of 432 in algae (Williams, 1990) and up to 1,000 in phytoplankton in rivers (Hameed et al., 1997).

In Ohio, soil and sediment exceeding total radium activity of 5 pCi/g must be disposed of in a radioactive waste facility (Ohio Admin. Code § 3701:1-43-15, 2017). Municipal landfill limits for technologically enhanced naturally occurring radioactive material (TENORM) in the United States range from 185 to 1,850 Bq/kg (5 to 50 pCi/g) (Smith et al., 2003).

#### Case Studies of Radium Accumulation in Blacklick Creek in Western Pennsylvania

In the spring of 2011, the Pennsylvania Department of Environmental Protection (PADEP) requested that unconventional well operators cease sending produced water from the Marcellus Formation to wastewater treatment facilities that were allowed to discharge high-saline effluents. Although participation was voluntary, treatment of Marcellus produced water at many wastewater treatment plants in Pennsylvania mostly ended by the fall of 2011 (Olmstead et al.,

2013). However, these facilities continued to receive, treat, and dispose produced water from conventional wells to local streams (Olmstead et al., 2013).

Between 2006 and 2011, brine was discharged from two centralized waste treatment facilities to Blacklick Creek in Western Pennsylvania (Burgos et al., 2017) containing Marcellus Shale brine. Between 2010 and 2011, approximately 50% of the brine was from the Marcellus Shale with the remainder from conventional oil and gas wells (Warner et al., 2013). Blacklick Creek merges into the Conemaugh River and discharges into the Conemaugh River Lake, a dam-controlled reservoir, approximately 19 km downstream of the discharge point (Burgos et al., 2017). The larger of the two facilities is the Josephine Brine Treatment Facility. The treatment process at the facility consisted of  $\text{Na}_2\text{SO}_4$  to remove metals and radium as a solid precipitate (Ferrar et al., 2013). Treated wastewater from the facility was released at a rate of ~0.585 million liters per day (MLd) (Warner et al., 2013). The average flow rate of Blacklick Creek is 756 MLd (Warner et al., 2013).

In a study conducted by Warner et al. (2013), concentrations of chloride and bromide in effluent to Blacklick Creek ranged from 55,000 to 98,000 mg/L and 474 to 1,266 mg/L, respectively (Warner et al., 2013) reflecting little or no treatment of salts. Bromide was enriched in surface water by a factor of 37X 1.8 km of discharge. Barium and radium concentrations in effluent indicated over 99% reduction relative to initial brine concentrations. The total activity of radium ( $^{226}\text{Ra} + ^{228}\text{Ra}$ ) in effluent was well below the industrial discharge limit of 2.2 Bq/L (60 pCi/L) in the United States (Warner et al., 2013). In August 2011, the  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio of effluent was 0.39 and  $^{87}\text{Sr}/^{86}\text{Sr}$  ranged from 0.7101 to 0.7111 consistent with Marcellus produced water (Warner et al., 2013). In June 2012, the  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio was 0.69 consistent with produced water for conventional oil and gas development in Pennsylvania (Warner et al., 2013) indicating curtailment of Marcellus Shale produced water disposal after 2011. The maximum activities of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in sediment were 8,732 and 2,072 Bq/kg collected within 10 m of the effluent outlet compared to upstream values of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  between 27–34 and 24–33 Bq/kg, respectively (Warner et al., 2013). Hence, despite reduction in Ra activity in the discharge water below the industrial discharge limit, significant Ra accumulation occurred in Blacklick Creek sediments because Ra has accumulated in sediments locally at the discharge site. Also,  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio measured in the river sediments at the discharge site (0.22–0.27) was consistent with ratios reported for Marcellus flowback and produced water and lower than the ratios recorded in all other background sediment samples throughout western PA (0.56–0.97) (Warner et al., 2013).

In 2015, sediment was excavated from Blacklick Creek up to 200 m (656 ft) downstream of a centralized waste treatment facility (Van Sice et al., 2018). Prior to remediation, radium activity in sediment was measured up to 7,400 Bq/kg with  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios ranging from 0.22 to 0.47 indicating impact from produced water from unconventional gas development (Van Sice et al., 2018). Following remediation, maximum radium activity was reduced to 407 Bq/kg. However, in 2017, radium activity in the remediation area increased up to 1,591 Bq/kg with a  $^{228}\text{Ra}/^{226}\text{Ra}$

ratio of 0.82 suggesting produced water from conventional oil and gas development as a causative factor and the need for further remediation (Van Sice et al., 2018).

Burgos et al. (2017) collected sediment and sediment pore-water samples from the Conemaugh River Lake, a dam-controlled reservoir, downstream of Conemaugh River and a tributary to the river, Blacklick Creek, which received produced water from two centralized waste treatment (CWT) facilities (19 km, or ~12 mi from the reservoir) from conventional and unconventional oil and gas wells on western Pennsylvania. Peak sediment concentrations of strontium, barium, and radium occurred at depths corresponding to peak unconventional produced water discharge (2006–2010) based on discharge records and sediment dating using lead-210 and beryllium-7 isotopes. This sediment depth had the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.710–0.711) in porewater indicative of Marcellus shale produced water (higher ratios reflective of background surface water and mine-impacted water). This sediment depth also corresponded to maximum total radium ( $^{226}\text{Ra}+^{228}\text{Ra}$ ) (4.7 pCi/g) activities (~200 times greater than background) and ratios of  $^{226}\text{Ra}/^{228}\text{Ra}$  (maximum 2.5) indicative of Marcellus Shale produced water reflecting higher uranium/thorium host rock where progeny of uranium and thorium are  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , respectively. Elevated concentrations of radium were detected ~19 km downstream of discharge indicating extensive impact. Also, nonylphenol ethoxylates (identified by non-targeted analysis using liquid chromatography time-of-flight mass spectrometry) were detected in sediment extracts at depths corresponding to dates of Marcellus Shale produced water discharge. Nonylphenol ethoxylates biodegrade to nonylphenol, a persistent endocrine disrupting compound. Thus, discharges of produced water can have far-reaching effects, and thereby affect ecosystems or receptors much farther than the immediate discharge area.

The previously described studies are inconsistent with a study conducted by Skalak et al. (2014), who examined radium concentrations in sediment up and downstream (generally less than 5 km, or ~3 miles) from the outfalls of five publicly owned treatment works (POTWs) in southwestern Pennsylvania that accepted Marcellus Shale wastewater between 2006 and 2011. Skalak et al. (2014) concluded that discharges from POTWs did not result in accumulation of radium in sediment at studied locations. However, they acknowledged that contaminated sediments may have been transported downstream from the areas that they sampled. Given Burgos et al. (2017) observed transport of contaminants 19 km (~12 mi) downstream, in a geomorphically identical area, it is likely that contaminated sediments were transported downstream from the sampled areas. Thus, this discrepancy may be due to the study's area of review rather than the absence of contamination accumulation.

In another study, Lauer et al. (2018) examined radium accumulation near the “Josephine Facility” near Josephine, PA which discharges treated produced water to Blacklick Creek and at two other facilities – the “Franklin Facility” in Franklin, PA which discharges treated produced water to the Allegheny River, and the “Hart Facility” in Creekside, PA which discharges treated produced water to the McKee Run. Treatment of produced water from the Marcellus Shale at these facilities diminished after 2012 but discharge of high salinity produced water from

conventional oil and gas well continued.

Warner et al. (2013) reported that  $^{226}\text{Ra}$  activity in the effluent from the Josephine Facility ranged from 0.13–0.19 Bq/L (3.5–5.1 pCi/L). Lauer et al. (2018) found  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity from the Franklin Facility at 0.4 (11 pCi/L) and 0.6 Bq/L (16 pCi/L), respectively in 2015. However, despite relatively low  $^{226}\text{Ra}$  activities in effluent, radium accumulated in sediment at high levels. Lauer et al. (2018) found  $^{226}\text{Ra}$  in sediment near the effluent outfall ranging from 269–14,949 Bq/kg (n=10) at the Franklin Facility and  $^{226}\text{Ra}$  activity from 119–10,747 Bq/kg (n=12) near the effluent outfall at the Josephine Facility. Upstream  $^{226}\text{Ra}$  activity near these facilities ranged from 9–41 Bq/kg (n=18). Radium accumulation at the Hart Facility was more modest at 57–351 Bq/kg (n=4). In addition to elevated  $^{226}\text{Ra}$  activity, Lauer et al. (2018) observed elevated lead-210 (progeny of  $^{226}\text{Ra}$ ) and thorium-228 (progeny of  $^{228}\text{Ra}$ ) in sediment at these two facilities at up to 1,593 and 4,591 Bq/kg, respectively. Upstream lead-210 and thorium-228 ranged from 14–81 Bq/kg and 9–38 Bq/kg. Thorium-228 is an alpha particle emitter with a half-life of 1.9 years while lead-210 is a beta particle emitter with a half-life of 22.2 years. Based on examination of ratios of thorium-228/radium-228, Lauer et al. (2018) concluded that  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , lead-210, and thorium-228 accumulation in sediment was due to conventional produced water disposal, calling into question the safety of produced water disposal in streams even at low radium levels.

McDevitt et al. (2019) detected  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity at levels up to 2,690 and 764 Bq/kg, respectively ( $^{226}\text{Ra} + ^{228}\text{Ra} = 3,454$  Bq/kg) in sediment from unidentified ephemeral streams in Wyoming where treatment of produced water from hydraulically fractured wells was limited to oil-water separation. Aqueous activities of  $^{226}\text{Ra}$  were below the 60 pCi/L regulated value (most below 10 pCi/L) with the highest detected level of  $^{226}\text{Ra} + ^{228}\text{Ra}$  activity at 57.2 pCi/L which was > 170X the upstream background level of  $^{226}\text{Ra} + ^{228}\text{Ra}$  activity at 0.33 pCi/L. While radium activities in sediment decreased rapidly with distance from effluent locations, radium activity in sediment remained above background levels of 40 Bq/kg greater than 20 km downstream of discharge points. Sediment cores at locations of elevated radium activity, indicated radioactive activity levels above background to the depth of coring (35 cm). Sequential extraction, mineralogical analysis, and geochemical modeling indicated that radium was primarily co-precipitated with calcium carbonates with smaller fractions associated with iron and manganese oxides indicating pH sensitivity of release (pH reduction induces release). As legacy acidic mine drainages are a common feature to Ohio River Basin streams (Sams III & Beer, 2000), these discharges may lead to geochemical shifts which are conducive to a release of radium from alluvial sediments.

In the Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings (40 CFR Part 192, 1995),  $^{226}\text{Ra}$  in the top 15 cm of surface soils in inactive uranium and thorium processing sites should not exceed 185 Bq/kg (5 pCi/g) above background concentrations and not exceed 555 Bq/kg (15 pCi/g) above background below 15 cm of the surface in any 100 m<sup>2</sup> area. These regulatory limits were exceeded at several locations in ephemeral streams in



Wyoming studied by McDevitt et al. (2019). Using first-order kinetics, a reduction of  $^{226}\text{Ra}$  from 2,690 to 225 Bq/kg (185+40 Bq/kg) will take almost 6,000 years. Warner et al. (2013) detected  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  at even higher activities of 8,759 and 2,187 Bq/kg (both >2 orders of magnitude above background), respectively in sediment near the effluent of a wastewater treatment plant in western Pennsylvania.

These investigations have revealed that radium accumulates in sediment downstream of produced water effluent at concentrations that exceed federal standards. The half-life of  $^{226}\text{Ra}$  is 1,600 years, indicating that past disposal of radium containing produced water can potentially impact human and ecological receptors for thousands of years.

#### Estimate of Radium Accumulation Following a Catastrophic Spill

Lauer et al. (2018) conducted mass balance calculations to demonstrate the accumulation of radium in sediment from disposal of produced water containing radium. Utilizing their approach, we can estimate radium accumulation in 3 cm of sediment following a catastrophic release of produced water from a single 10,000-barrel (420,000 gallons) barge unit (202.4 x 46 ft) (Settoon Towing). Assuming a median  $^{226}\text{Ra} + ^{228}\text{Ra}$  activity of 2,460 pCi/L (91.1 Bq/L) (Rowan et al., 2011), the total radium activity would equal  $1.45 \times 10^8$  Bq. Depending on the spread of radium (1 to 4 barge areas considered here), radium concentration in sediment would vary from 186 to 5,582 Bq/kg assuming a sediment density of  $1.0 \text{ g/cm}^3$  (Lauer et al., 2018). While there are no federal regulations governing the removal of radium from soil or sediment, several states have developed limits ranging from 185 to 1,850 Bq/kg (Smith et al., 2003). Hence, in the event of a release of even a portion of the capacity of a barge holding produced water, sediment removal could be required. A larger spill would almost certainly require excavation.

Van Sice et al. (2018) found elevated (up to ~1.5 times background) radium activity in sediment in Blacklick Creek 31 km (~19 mi) downstream of a centralized waste facility where sediment remediation had occurred in 2015. Similar to findings by Burgos et al. (2017), the findings of Van Sice et al. (2018) indicated that radium can be transported a significant distance downstream of a point of discharge. Consequently, legacy impacts following catastrophic releases of radium-rich produced water are possible and may even persist following remediation activities. In short, discharges of radium-rich produced water have the potential to impact areas disproportionate to the immediate spill zone, and possibly on timescales ranging from decades to centuries or longer.

#### **Conclusion**

The lack of disclosure of additives used for oil and gas production in all states except California is limited to hydraulic fracturing. There is considerable overlap between additives used for hydraulic fracturing and additives used for acid stimulation and conventional oil and gas development. Even when chemical disclosure occurs, self-reporting is voluntary in most states and is limited to non-proprietary compounds and additives. Additives without CASRNs are often provided, making chemical identification challenging. Complete disclosure of all chemicals used for all oil and gas development is necessary because produced water disposal has the potential to

impact human or ecological receptors.

Chemical analysis performed at commercial laboratories using standard USEPA methods indicates elevated concentrations of compounds of concern such as benzene and radionuclides such as radium, both known human carcinogens, are present in produced water. Furthermore, produced water is known to contain bioaccumulative chemicals of concern (e.g., mercury, lead), and spills of produced water would be directly analogous to the mixing zones that the Ohio River Valley Water Sanitation Commission has sought to eliminate (ORSANCO, 2015). High levels of total dissolved solids and organic matter can cause matrix interference using standard USEPA methods resulting in a negative bias in detection and quantification. Furthermore, in addition to stressing aquatic ecosystems, the high concentrations of total dissolved solids present in produced waters could also potentially mobilize pools of legacy metal contamination associated with the industrial history of the Ohio River Valley. A recent study by Bonetti et al. (2021) found impacts to surface water across the United States resulting from unconventional oil and gas development. These findings reinforce the observation that unconventional oil and gas development causes impacts to surface water and sediment, and these impacts could be exacerbated by transporting produced water by barge.

Equally concerning is the current inability to identify and quantitate numerous other compounds in produced water making risk assessment problematic. While significant advancements have been made in identifying compounds in produced water using research-based analytical methods, compound identification is still in a nascent phase, and these methods are not available at commercial laboratories for widespread utilization.

To evaluate the risk posed by spills of produced water in the Ohio River, comprehensive analysis of produced water is necessary. Even in the presence of complete disclosure of additives, biotic (e.g., biodegradation) and abiotic (e.g., oxidation) transformation of organic compounds will occur both downhole and above ground during storage. These compounds will not be detected using standard USEPA methods. Given that new additives are being continuously introduced to support oil and gas extraction, full identification and quantification of organic compounds in produced water is a challenging objective.

Compounding issues associated with the identification and quantification of compounds in produced water is the fact that little is known about the physicochemical, biological, and toxicological properties of many compounds known to be used for oil and gas production and present in produced water. Many organic compounds released to surface water will undergo biotransformation. Other compounds may accumulate in sediment. Fate and transport properties of compounds and associated transformation products present in produced water must be known to evaluate the risk of impact to human and ecological receptors. Chronic oral reference doses and cancer oral slope factors are lacking for many compounds known to be used for oil and gas development and present in produced water precluding defensible risk assessment. Further development and routine use of bioanalytical methods (e.g., endocrine disruption) are necessary to ensure the safety of discharging produced water to surface water.

Another concern is the generation of carcinogenic disinfection byproducts at drinking water intakes downstream of produced water spills due to elevated levels of bromide and ammonium. Drinking water plants downstream of produced water effluent (e.g., Pittsburgh Water and Sewer Authority) have already noted a shift in bromated disinfection byproducts. This shift has occurred from relatively diluted releases of produced waters. Concentrated releases of produced water, due to spill events, likely will result in more dramatic shifts in bromated disinfection byproducts and may prove more costly or difficult to adequately address.

In summary, produced waters of the Appalachian Basin are known to contain toxic inorganic, organic, and radiogenic constituents, that can have negative impacts on both humans and river ecosystems. However, the full suite of organic compounds in produced water cannot be identified and quantified. Thus, it is nearly impossible to identify all potential impacts to human and ecological receptors resulting from produced water spills, and we cannot fully constrain the risk that barging operations pose. Accidental releases of produced waters, whether catastrophic or chronic, likely can seriously impair either of these receptors, and will likely prove difficult (at best) and costly to remediate.

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