

Evaluation of the Draft EPA Report “Study of Oil and Gas Extraction Wastewater Management Under the Clean Water Act (EPA- 821-R19-001), May 2019”

Dominic DiGiulio, PhD¹

Lee Ann Hill, MPH¹

Seth B.C. Shonkoff, PhD, MPH^{1,2,3}

¹ PSE Healthy Energy

² Department of Environmental Science, Policy and Management, University of California, Berkeley

³ Lawrence Berkeley National Lab

July 1, 2019



Purpose

In this report we evaluate and provide technical comments on the draft EPA report entitled, “Study of Oil and Gas Extraction Wastewater Management Under the Clean Water Act (EPA-821-R19-001), May 2019”.

About PSE Healthy Energy

Physicians, Scientists, and Engineers for Healthy Energy (PSE Healthy Energy) is a multidisciplinary, non-profit energy science and policy research institute that studies the way energy production and use impact public health and the environment.

Funding

Funding for the drafting of this report was provided by Earthjustice.

About the Authors

Dominic DiGiulio, PhD

Dr. Dominic DiGiulio is a senior research scientist at PSE Healthy Energy. Dr. DiGiulio completed a B.S. in environmental engineering at Temple University, an MS in environmental science at Drexel University, and a PhD in soil, water, and environmental science at the University of Arizona. During his 31 years with the U.S. Environmental Protection Agency’s Office of Research and Development, Dr. DiGiulio conducted research on gas flow-based subsurface remediation (soil vacuum extraction), soil-gas sampling methodology, gas permeability testing, intrusion of subsurface vapors into indoor air (vapor intrusion), subsurface stray gas (methane and carbon dioxide) migration, and solute transport of contaminants in soil and groundwater including that associated with hydraulic fracturing. He assisted in development of guidance of EPA’s original guidance on vapor intrusion and the EPA Class VI rule on geologic sequestration of carbon dioxide. The focus of Dr. DiGiulio’s current work is on human health and environmental aspects of oil and gas development in the United States and abroad.

Lee Ann Hill, MPH

Lee Ann Hill joined PSE Healthy Energy in 2016 as part of the Environmental Health Program. Lee Ann has worked in academic, advocacy, industry, and government settings on topics related to energy, material safety, and public health. Her research has focused on environmental and human health impacts of oil and gas and chemical fate and transport. Lee Ann received her Master’s in Public Health from University of California, Berkeley with a concentration in

Environmental Health Sciences. She also holds her Bachelor's in Environmental Science from Ithaca College with a concentration in Pollution Science: Local and Global Perspectives.

Seth B.C. Shonkoff, PhD, MPH

Dr. Seth Shonkoff is the executive director of the energy science and policy institute, PSE Healthy Energy. Dr. Shonkoff is also a visiting scholar in the Department of Environmental Science, Policy and Management at UC Berkeley and an affiliate in the Environment Energy Technology Division at Lawrence Berkeley National Laboratory in Berkeley California. An environmental and public health scientist by training, he has more than 15 years of experience in water, air, climate, and population health research and has published more than 35 peer-reviewed journal articles and reports. He has worked and published on topics related to the intersection of energy, air pollution, water quality, climate, and human health from scientific and policy perspectives. Dr. Shonkoff has co-authored multiple high-profile scientific assessments including the Human Health chapter of The Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5), two human health chapters in the California Senate Bill 4 independent scientific study on hydraulic fracturing and well stimulation; and an assessment of the public health dimensions of underground gas storage in the State of California. Dr. Shonkoff serves on multiple science-policy expert panels and in 2018 was awarded as one of 20 Pioneers in Environmental Public Health under 40 by the Collaborative on Health and the Environment. Dr. Shonkoff completed his PhD in the Department of Environmental Science, Policy, and Management and his MPH in epidemiology in the School of Public Health from the University of California, Berkeley.

Background

Throughout 2018, the United States Environmental Protection Agency (EPA) contacted individuals from state regulatory agencies, the oil and gas industry, academia, and non-governmental organizations (NGOs) (collectively referred to as stakeholders) to better understand “barriers and concerns” associated with increasing onshore produced water discharge opportunities under the Clean Water Act (CWA) (EPA 2019). During this time, the EPA also created a public docket (Regulations.gov 2018) for submittal of written comments and conducted a public meeting in Washington D.C. on October 9, 2018 (EPA 2018a) to gather additional feedback from stakeholders. The results of this survey were released in a draft report in May 2019 entitled “Study of Oil and Gas Extraction Wastewater Management Under the Clean Water Act” (EPA 2019). The EPA is now requesting public comment on this report.

Most produced water in the United States is disposed of using Class II Underground Injection Control (UIC) disposal wells. The EPA states that limitations of this practice are “evident in some areas” (referring to over-pressurization of UIC disposal wells and induced seismic activity from disposal of produced water) and that “new approaches” are necessary (EPA 2019).

Under 40 CFR 435 Subpart C, the direct onshore discharge of produced water to surface water must meet an Effluent Limitation Guideline (ELG) of “zero discharge” of pollutants (EPA 2019). This zero discharge ELG has essentially resulted in a prohibition of direct discharge of produced water to surface water under 40 CFR 435 Subpart C. However, 40 CFR 435 Subpart C allows the indirect discharge of produced water to surface water through publicly owned treatment works (POTWs) (EPA 2019). In 2016, the EPA prohibited the indirect discharge of produced water from unconventional wells to POTWs (88126 Federal Register). Indirect discharge of produced water from conventional wells to surface water through POTWs occurs primarily in Pennsylvania (EPA 2019). There are no pretreatment standards for indirect discharge to POTWs (EPA 2019).

Produced water can be directly or indirectly discharged to surface water under 40 CFR 435 in Subparts E, F, and H. Under 40 CFR 435 Subpart E, produced water can be discharged directly to surface water if production wells are located west of the 98th meridian and produced water “is of good enough quality to be used for wildlife or livestock watering or other agricultural uses and that the produced water is actually put to such use during periods of discharge.” The 98th meridian extends from near the eastern edge of the Dakotas through central Nebraska, Kansas, Oklahoma, and Texas.

Discharge of produced water into surface water under 40 CFR 435 Subpart E occurs primarily in Wyoming (EPA 2019). Approximately 30% of oil field produced waters under 40 CFR 435 Subpart E in Wyoming are discharged into surface waters (Ramirez 2002). In 1997, about 55,000 acre-feet (AF) or 18 billion gallons (325,851 gallons = 1 AF) of oil field produced water was discharged into surface water (Ramirez 2002). The ELG for discharge under 40 CFR 435 Subpart E is limited to an oil and grease concentration ≤ 35 mg/L, however, in Wyoming, the

effluent limit for oil and grease is typically 10 mg/L (Ramirez 2002). In general, treatment of produced water prior to discharge in Wyoming is limited to settling of suspended solids and skimming of oil (EPA 2019). Heat is generally used by the operator to separate oil from water (Ramirez 2002). Produced water is then discharged into unlined earthen-diked skim ponds or pits for further oil-water separation prior to discharge into wetlands or riparian areas (Ramirez 2002). In oil fields having high produced water to oil ratios, production would likely not be viable if treatment of produced water beyond oil-water separation and settling was required prior to discharge to surface water (McDevitt et al. 2018).

The Wyoming Department of Environmental Quality (WDEQ) partitions surface water into four classes. Class 1 surface water supports all uses. No water quality degradation nor discharge is permissible. Class 2 surface water supports or can support game fish or nurseries. Class 3 surface water supports or can support nongame fish. Class 4 surface water includes all intermittent and ephemeral stream and does not support fish. Over one-half of discharges under 40 CFR 435 Subpart E occurs in Class 4 surface water (Ramirez 2002). There is limited information available from on-line data systems to indicate characteristics of 40 CFR 435 Subpart E facilities, such as the types of waste accepted (EPA 2018b). In some drainages, oil field produced water accounts for up to 89% of stream flow (Boelter et al. 1992).

Under 40 CFR 435 Subpart F, produced water can be discharged directly to surface water if production wells produce ≤ 10 barrels of crude oil per day (i.e. stripper wells). Discharge under 40 CFR 435 Subpart F was not considered in this report.

Under 40 CFR 435 Subpart H, produced water from coal bed methane (CBM) recovery wells can be discharged directly to surface water. Approximately 45% of produced water from CBM recovery is discharged to surface water (EPA 2010). Most of the remaining produced water from CBM recovery is discharged to percolation ponds or applied to land (EPA 2010). In 2008, 66,115 AF or ~21.5 billion gallons of produced water from CBM wells was discharged to surface water with most discharge occurring in the Powder River Basin in Wyoming (67.9%), the Raton Basin in Colorado (11.7%), the Black Warrior Basin in Alabama (11.4%), the Powder River Basin in Montana (5.9%), and with remaining discharge in the Green River Basin in Wyoming (1.4%), the Cahaba Basin in Alabama (1.1%), the Illinois Basin in Illinois and Indiana (0.5%), and the Appalachian states (0.1%) (EPA 2010). Hence, in 2008, most discharge of CBM water occurred in the Powder River Basin (73.8%) (48,762 AF or ~15.9 billion gallons) and in the State of Wyoming (69.3%) (45,878 AF or ~14.9 billion gallons).

We could not find an estimate of the total volume of produced water discharged into surface water under 40 CFR 435 Subparts E and H in Wyoming. However, estimates under 40 CFR 435 Subpart E by Ramirez (2002) and under 40 CFR 435 Subpart H by EPA (2010) indicate that total discharge of produced water into surface water could exceed ~100,900 AF or ~33 billion gallons per year in Wyoming.

There are no ELGs for 40 CFR 435 Subparts F and H. Technology-based limitations are developed on a case-by-case basis or through a state-wide general permit for non-stripper and CBM production wells. However, direct discharge to surface water under 40 CFR 435 Subparts E, F, and H require issuance of permits under the National Discharge Elimination System (NPDES) by EPA or a state regulatory agency (EPA 2019). The most frequently monitored parameters under 40 CFR 435 Subpart H are pH, chloride, total suspended solids, total dissolved solids (TDS), sodium adsorption ratio (SAR), oil and grease, and metals (EPA 2010). Alabama, Colorado, and Wyoming also include acute whole effluent toxicity (WET) testing of effluent under Subpart H (EPA 2010).

Under 40 CFR Part 437, produced water from both conventional and unconventional oil and gas development can be indirectly discharged to surface water via centralized waste treatment (CWT) facilities. CWT facilities are primarily located in the Marcellus and Utica shale areas of Pennsylvania, Ohio and West Virginia (EPA 2019). Treatment of produced water at CWT facilities varies from simple physical/chemical treatment to advanced treatment utilizing membrane technology or distillation (EPA 2019).

NPDES permits for discharge from POTWs, CWT facilities under 40 CFR Part 437, and under 40 CFR Part 435 Subparts E, F, and H contain requirements for discharge monitoring reports which include the frequency for collecting wastewater samples, the location for sample collection, the pollutants to be analyzed, and the laboratory procedures to be used in conducting the analyses. When ELGs are not sufficiently protective, additional, more stringent water quality-based effluent limits (WQBELs) can be included in NPDES permits. In addition to containing WQBELs, NPDES permits can also contain provisions for additional monitoring of sediment and fish tissue. Hence, a permitting agency has considerable flexibility and authority in protecting human and ecological receptors if desired.

The EPA has delegated issuance of NPDES permits to most states. EPA still issues NPDES permits in six states (Idaho, Massachusetts, New Hampshire, New Mexico, Oklahoma and Texas) as well as certain territories and tribal lands. In anticipation of increased surface water disposal opportunities for produced water, Texas, Oklahoma, and New Mexico are seeking permission from EPA to issue NPDES permits (Lee 2018). The Texas legislature is in the process of transferring responsibilities of produced water reporting from the Railroad Commission of Texas (RRC) to the Texas Commission on Environmental Quality under Texas House Bill 2771 to enable the TCEQ to seek NPDES delegation from EPA (Gromatzky 2019). The RRC has asked EPA's Administrator, Andrew Wheeler, for assistance obtaining permitting authority for oil and gas wastewater (Lee 2018).

Individuals from some state agencies and the oil and gas industry (e.g., Domestic Energy Producers Alliance 2018) want produced water re-branded as a "resource" rather than a "waste" product. Individuals from some state agencies questioned whether it made sense to "waste" this water "resource" especially in arid regions of the country (EPA 2019).

EPA stated in its draft report that industry was generally supportive of increasing discharge options under the CWA. Individuals from industry stated that expanded discharge opportunities would increase the ability to “economically manage” the cost of produced water disposal and “positively affect the economics of oil and gas extraction” in some areas. Individuals from industry also stated that with expanded opportunities to discharge produced water to surface water, they wanted NPDES permits to be issued in a more expedited manner and with greater flexibility. However, a major unidentified producer did not support increased discharge options because of “lack of science around treatment efficiency and associated liability risks” (EPA 2019).

Individuals from some states did not support expanding discharge opportunities for produced water citing uncertainty in identification of chemical constituents and associated transformation products and toxicity (EPA 2019). These individuals also expressed concern regarding the disposal of residuals following treatment of produced water especially technologically enhanced naturally occurring radioactive materials (TENORM). Personnel from some state agencies said that they lacked the technical expertise to issue NPDES permits for complicated waste streams such as produced water and that water quality standards did not exist for many compounds in produced water making issuing NPDES permits problematic (EPA 2019).

In the draft EPA report, EPA stated that scientists from NGOs and academia had a number of concerns regarding the expanding discharge opportunities under the CWA including the following. (1) There is a need to better identify chemical constituents in produced water. Many compounds used during well development are proprietary. Chemical formulations used for well development are constantly changing as new chemicals enter the market. Transformation of chemical constituents occur downhole. Analytical methods do not exist for many compounds. (2) A large number of chemical compounds used in exploration and production have little data on toxicity. Water quality criteria do not exist for many constituents. (3) There is limited treatment technology performance data for many compounds known to be present in produced water. (4) For discharges to intermittent and ephemeral streams, there is no safety factor provided by dilution.

Upon finalizing this draft EPA report, the EPA stated that it will determine “next steps for produced water management” and better use of this “resource” under the CWA. The EPA has stated that these “next steps” will include the development of “additional discharge options under the CWA for onshore oil and gas wastewater.” The EPA’s public declaration of its intent to pursue changes in the CWA to facilitate discharge of produced water to surface water has led to speculation as to what these “next steps” could be.

Saunders (2019) states that the EPA may attempt the following changes to the CWA to allow additional discharge opportunities: (1) eliminate the zero discharge prohibition under 40 CFR 435 Subpart C, (2) revisit the ban on discharge of unconventional produced water to POTWs, (3)

extend the vague “good enough quality” standard of 40 CFR 435 Subpart E nationwide, and/or (4) weaken standards for CWT facilities.

Based upon a review of EPA’s draft report, arguments for the increased discharge of produced water to surface water made by industry and some states are flawed. Also, there are considerable existing concerns regarding the safety produced water disposal into surface water that expanded discharge would significantly worsen. An explanation of these concerns follows.

The Chemical Composition of Produced Water Needs to be Better Characterized

The identification of chemical constituents in produced water begins with requirements for disclosure of chemical additives used downhole during oil and gas development. EPA identified 692 unique ingredients reported for additives, base fluids and proppants contained in more than 39,000 FracFocus disclosures (EPA 2015). 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). It is unclear why disclosure for chemicals used during hydraulic fracturing is not required in all oil and gas producing states.

Disclosure when required is limited to chemicals that are not considered proprietary which introduces significant uncertainty to risk assessment. Stringfellow et al. (2017a) reviewed 1,623 hydraulic fracturing treatments entered into FracFocus for 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 propriety. 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 acid stimulation (Abdullah et al 2017, Shonkoff et al. 2015). However, California is the only state that requires disclosure of chemicals used for acid well stimulation treatments (matrix acid stimulation and acid fracturing). There is also considerable overlap between compounds used for hydraulic fracturing and routine production well activities (Stringfellow et al. 2017b). 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 necessary if the endpoint of produced water is discharge to surface water, use for irrigation, road spreading, or any other pathway that could involve human or ecological receptors. Disclosure of chemicals used for all phases of well development would better inform the scientific community, regulatory agencies, and the public about potential risks posed by chemical

additives. In the draft EPA report, EPA mentioned that individuals from industry stated proprietary compounds are non-toxic. In the absence of actual disclosure, this statement cannot be verified.

While 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, comprehensive analysis of treated wastewater prior to discharge to surface water is necessary to characterize potential risk posed to human health and ecological receptors posed by these discharge activities. Produced water has been analyzed for inorganic composition (major ions, heavy metals, and radioactive elements) and to some extent for known organic additives at commercial laboratories. 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 polyaromatic hydrocarbons, and elevated levels of radionuclides such as radium which is also a known human carcinogen.

Produced water can contain total organic carbon (TOC) levels greater than 1500 mg/L with only a minor portion of TOC characterized by standard EPA methods (Rosenblum et al. 2017). In its 2016 national report on hydraulic fracturing, the EPA listed 1,606 chemicals that were reported to be used in hydraulic fracturing or detected in produced water of hydraulically fractured wells (Appendix H, EPA 2016). Additionally, the EPA 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. The EPA 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” (Ch 7, EPA 2016). In addition, the identification and quantification of organic compounds in produced water can be challenging because of matrix effects (Nell and Helbling 2018). The complex nature of produced water also interferes with detection of naturally occurring radioactive material (NORM), Nelson et al. (2014) found that matrix effects (high ionic strength) in produced water could decrease recovery of radium-226 (^{226}Ra) to just 1% of that present.

Comprehensive analyses and characterization of organic compounds present in flowback and produced water is only in nascent stages. The use of innovative analytical methods has resulted in the detection of organic compounds not routinely analyzed for or detected using standard EPA methods at commercial laboratories. Advanced methods for detection of organic compounds includes high performance liquid chromatography with tandem mass spectrometry (HPLC–MS/MS) (DeArmond and DiGoregorio 2013a, b), liquid chromatography quadrupole time-of-flight mass spectrometry (LC/Q-TOF-MS) (Ferrer and 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).

Given the uncertainty of produced water quality characterization, full identification of compounds in produced water and associated toxicity is necessary to evaluate the effectiveness of wastewater treatment approaches prior to discharge to surface water. 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 for at commercial laboratories and is not effectively removed by conventional wastewater treatment. ADBAC has been detected in surface water and sediment downstream wastewater sources (Ferrer and Furlong 2001, 2002).

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 and Hoelzer 2016). Alkoxyated nonylphenols, disclosed in ~50% of hydraulic fracturing treatments, biodegrade to the relatively persistent endocrine disrupting compounds octylphenol and nonylphenol (Elsner and Hoelzer 2016). Leuk 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).

EPA has stated that approved analytical methods do not exist for many constituents found in oil and gas extraction wastes (EPA 2018b). EPA has stated further that some constituents (such as total dissolved solids) found in oil and gas extraction wastes can interfere with EPA approved analytical methods and significantly affect the ability to detect and quantify the level of some analytes (EPA 2018b). In its May 2018 report on CWT facilities, EPA also stated that there is a “primary data gap” in understanding the composition of produced water accepted at CWT facilities and the basis of NPDES permits. The EPA acknowledged that it had little understanding of how NPDES permits were being issued at CWT facilities and whether permits were sufficient for effectively treating produced water (EPA 2018b).

Statements by the EPA 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 EPA 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.

The potential impact of discharge of produced water to human and ecological receptors cannot be evaluated if the full suite of compounds in produced water cannot be identified and quantitated. Expanding discharge options under the CWA magnifies this concern.

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 (Stringfellow et al. 2014, 2017a, b, Elsner and Hoelzer 2016, Rogers et al. 2015). 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 EPA draft report, the EPA stated that some scientists from academia expressed concern that there is little data on the fate of compounds in produced water. Hence, this issue is broadly recognized. 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 to surface water.

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 South Coast Air Quality Management District (SCAQMD, CA), Stringfellow et al. (2017) identified 525 chemical additives, 233 (44%) of which lacked CASRN and an additional 140 (27%) that lacked available toxicity data.

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 (2019), 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 remaining 139 compounds (36%) were evaluated for toxicity using authoritative lists and databases.

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 1076 (~8%) of compounds identified by EPA 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.

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, 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).

Whole Effluent Toxicity (WET) testing can be incorporated into NPDES permits to evaluate the aggregate toxic effect to aquatic organisms from all pollutants contained in wastewater effluent (EPA 2019b). WET tests measure wastewater's effects on specific test organisms' ability to survive, grow and reproduce (EPA 2019b). EPA provides approved methods for both acute and chronic freshwater testing (EPA 2019b). Both acute and chronic WET testing should be routinely incorporated into NPDES permits for produced water effluent.

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. 2018a, 2016, 2015, 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 et al. 2018b, 2016a, 2016b, Tasker et al. 2018).

The Discharge of Produced Water to Surface Water Presents a Risk to Human and Ecological Receptors

Field studies on wastewater treatment of produced water in Pennsylvania indicate exceedance of maximum contaminant levels and incomplete removal of organic compounds (Ferrar et al. 2013, Getzinger et al. 2015) prior to discharge to surface water. A large proportion of compounds used in routine oil and gas development operations and in hydraulic fracturing and acid treatments are acutely toxic to aquatic life (Shonkoff et al. 2015, Stringfellow et al. 2017b, Butkovskyi et al. 2017).

The EPA has stated that depending on the level of treatment, effluent from CWT facilities may contain elevated levels of TDS, halides, metals, and TENORM relative to the receiving streams into which they are discharged and that elevated concentrations of these constituents have been detected in aqueous samples collected downstream of CWT facility discharge points (EPA 2018). The EPA has also stated further that levels of pollutants downstream from CWT facility discharges have been reported to exceed applicable thresholds, such as primary and secondary drinking water standards and acute and chronic water quality criteria for protection of aquatic life. In a number of cases, CWT effluents have been shown to adversely affect downstream aquatic life and, in one case, have been shown to affect survival of a federally-listed endangered species (EPA 2018b).

In arid regions of the country, discharges will occur primarily to intermittent and ephemeral streams. Creation of a perennial stream from a historically ephemeral stream using produced water flows may create an unsustainable ecosystem, because as wells are abandoned, water sources will no longer be available (Guerra et al. 2011). In addition, dissolved organic material in produced water may deplete dissolved oxygen concentrations in surface water due to increased biological oxygen demand (Guerra et al. 2011).

Poor maintenance of skim ponds or pits in Wyoming under 40 CFR 435 Subpart E discharge has caused oil to remain on the water surface resulting in mortality of migratory birds and other wildlife (Esmoil and Anderson 1995). Ramirez (2002) surveyed skim ponds at 65 locations and collected effluent samples from skim ponds at 12 locations in Wyoming. Ramirez (2002) noted visible sheens at 15% of discharge locations and exceedance of the WDEQ standard of 10 mg/L oil and grease at 12 locations (83%) with a maximum concentration of 54.2 mg/L. WDEQ regulations prohibit the presence of a visible sheen in wastewater discharges (Ramirez 2002). Ramirez (2002) states that previous monitoring by the WDEQ indicated oil and grease concentration effluent at up to 130 mg/L. Ramirez (2002) also noted that approximately 15% of

surveyed locations had oil-stained vegetation and that oil stained sediment was visible immediately below the skim pond effluent at 44% of locations surveyed. Ramirez (2002) also noted that over 62% of locations surveyed had inadequate measures (flagging, fences only, or nothing) to exclude birds and wildlife from skim pits. Ramirez (2002) states that the U.S. Fish and Wildlife Service has observed large bird mortality events at skim ponds due to lack of use of adequate measures such as netting or closed containment systems.

The primary issues associated with the discharge of produced water from CBM development under 40 CFR 435 Subpart H are flow volume, salinity and toxicity. A high flow volume into a receiving stream can increase suspended sediment and streambed erosion (ALL 2003). Erosion can destroy vegetation within streams impacting aquatic biota that have particular flow requirements for food, habitat, and reproduction (ALL 2003). Saline discharges from CBM produced water can alter plant communities as native species are replaced with salt-tolerant species (ALL 2003). Other components in CBM produced water that are toxic to native plants and organisms are elevated concentrations of ammonia, hydrogen sulfide, bicarbonate, selenium, chloride, and boron (ALL 2003).

In the draft EPA report, scientists from NGOs expressed concern that the discharge of produced water to intermittent and ephemeral streams may enhance erosion and alter the vegetation or biota present in and adjacent to these streams. They stated further that these discharges provide little or no safety factor by dilution thereby increasing the risk of adverse effects from discharges. Given that the discharge of produced water to surface water is already impacting aquatic receptors, the expansion of discharge opportunities can only worsen this ongoing impact.

Of considerable concern is the buildup of radium deposited in sediment downstream of produced water effluent outfalls. Radium is a known human carcinogen associated with cancers of the breast, blood, bone, and liver (ASTDR 1999) with bioaccumulation factors in freshwater fish, invertebrates, mollusks, and shells ranging from 100-1000 (Warner et al. 2013). Ramirez (1993) found that bone tissue from birds inhabiting a wetland receiving produced water near Cody, Wyoming contained ^{226}Ra in addition metabolites of polyaromatic hydrocarbons in bile. The drinking water standard for $^{226}\text{Ra} + ^{228}\text{Ra}$ is 0.185 Bq/L (5 pCi/L). Most states allow a produced water discharge limit of 2.22 Bq/L (60 pCi/L) for ^{226}Ra (NRC 2017).

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 (IAEA 2014). However, radium can be released to a degree under sulfate reducing conditions (Ouyang et al. 2017, Renock et al. 2016, Phillips et al. 2001). Carbonates containing radium can dissolve in response to acidification (McDevitt et al. 2018).

McDevitt et al. (2018) detected ^{226}Ra and ^{228}Ra activity at levels up to 2,690 and 764 Bq/kg, respectively ($^{226}\text{Ra} + ^{228}\text{Ra} = 3,454 \text{ Bq/kg}$) 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}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).

In the Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings (40 CFR Part 192) (EPA 1995), ^{226}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 m² area. These regulatory limits were exceeded at several locations in ephemeral streams in Wyoming studied by McDevitt et al. (2018). Using first-order kinetics, a reduction of ^{226}Ra from 2,690 to 225 Bq/kg (185+40 Bq/kg) will take almost 6,000 years. Warner et al. (2013) detected ^{226}Ra and ^{228}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.

Akob et al. (2016) detected elevated ^{226}Ra in sediment near a Class II disposal well receiving hydraulic fracturing wastewater in West Virginia in which produced water was previously stored in impoundments. Kassotis et al. (2016a) and Orem et al. (2017) also investigated impact to this watershed with the former finding high levels of endocrine disrupting chemical activity in surface water extracts and the later finding numerous chemicals associated with hydraulic fracturing in surface water and sediment.

These investigations have revealed that radium accumulates in sediment downstream of produced water effluent that exceed federal standards. The half-life of ^{226}Ra is 1600 years indicating that past disposal of radium containing produced water can potentially impact human and ecological receptors for thousands of years. Any expansion of surface water disposal options for produced water would result in greater releases of radium to surface water and greater accumulation in sediment.

Another concern is the generation of disinfection byproducts 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. 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 (Richardson et al. 2008, Plewa et al. 2004) and are potentially tumorigenic (Wei et al. 2013). Elevated bromide concentration during chloroamination promotes the formation of the potent carcinogen N-nitrodimethylamine (NDMA) (Luh et al. 2012, Shah et al. 2012a, b).

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. Parker et al. (2014) also demonstrated that elevated levels of bromide and iodide during drinking water disinfections causes a shift in THM, HAN, and HNM formation toward brominated and iodinated analogues at wastewater volume fractions as low as 0.01%.

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 (EPA 2018b). 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 (EPA 2018b). Increasing discharge opportunities will increase the potential for ingestion and inhalation (through showering, laundry use, etc.) of toxicants and carcinogens from disinfected drinking water.

Treatment of Produced Water Prior to Discharge is Insufficient and Poorly Regulated

The range of pollutants present in produced water requires a multi-step treatment train process to meet discharge standards (EPA 2018b). However, treatment at CWT facilities is often limited to chemical precipitation which provides little or no removal of the many pollutants commonly found in produced water (EPA 2018b). Some CWT facilities discharge much greater quantities of pollutants, such as total dissolved solids and chlorides, than others (EPA 2018b).

Current ELGs in 40 CFR Part 437 promulgated in 2000 and amended in 2003 were developed prior to the dramatic increase in hydraulic fracturing after 2010 (EPA 2018b). As a result, ELGs in 40 CFR Part 437 do not contain limitations and associated treatment requirements for many of the pollutants commonly found in oil and gas wastewater (EPA 2018b). Many of these pollutants are not included on the current list of priority pollutants (EPA 2018b).

ELGs and treatment standards do not fully reflect constituents known to be in produced water. Given these limitations, the effectiveness of treatment cannot be evaluated. In the draft EPA

report, scientists from NGOs and academia were concerned that limited treatment technology performance data exists for compounds associated with produced water (EPA 2019). Individuals operating POTWs stated that they did not want to accept additional produced water from oil and gas production because the treatment technology utilized at POTWs is unsuitable for produced water. There are no pretreatment requirements for produced water currently being sent to POTWs from conventional oil and gas development. As previously discussed, many compounds in produced water from unconventional oil and gas development are also present in conventional oil and gas development.

There is a lack of clarity among oil and gas operators regarding applicability of the current CWT effluent guidelines to facilities that treat oil and gas extraction wastes (EPA 2018b). Some of this is centered on the interpretation of what constitutes an “off-site” facility. A facility must receive produced water from an offsite location to be regulated under 40 CFR Part 437. Because there is some room for interpretation of what constitutes “off-site” and “on-site” treatment, CWT facilities could be regulated under 40 CFR Part 437 or 40 CFR Part 435 in which regulation under the latter is governed by “best professional judgement” (EPA 2018b). Hence, some facilities that are currently regulated by 40 CFR 435 Subparts E, F, or H where “best professional judgement” is used to determine effluent limitations should be regulated under 40 CFR 437 where effluent limitations would be stricter although still not sufficiently protective. Also, some CWT facilities operate under expired permits or no permits at all (EPA 2018b). It is difficult to justify expansion of discharge opportunities under the CWA when current discharge is not properly managed.

Treatment of Produced Water for Discharge to Surface Water Leads to Generation of Toxic and Radioactive Residuals.

Brines produced from technologies such as reverse osmosis, evaporators, and crystallizers create residual containing high levels of salts (EPA 2018b). Disposal of these residuals in landfills has the potential to increase salinity of landfill leachate (EPA 2018b). The EPA has stated that the removal of barium and co-precipitation of radium from produced water may result in the generation of solid waste that exhibits “high levels of radioactivity that preclude disposal in most landfills” (EPA 2018b). Radium in sludge from the treatment of produced water can be as high as 244,200 Bq/kg (Smith 1992). Using first-order kinetics, a reduction of ^{226}Ra in sludge from 10,000 to 100 Bq/kg requires almost 11,000 years. Radioisotopes in wastewater treatment residuals disposed in landfills may be released to the environment through leachate (EPA 2018b).

Robust interstate tracking of the transport and disposal of radioactive waste material, especially that associated with wastewater and pond sludges and filter socks, should be an urgent priority for the EPA. As calculations using first-order kinetics for radioactive decay demonstrates, waste material associated with the storage and treatment of produced water will present a potential risk to human and ecological receptors for thousands of years into the future. It is difficult to justify

expanded discharge opportunities for produced water when radioactive waste materials may not be properly tracked and may not be adequately contained for thousands of years.

EPA or State Agencies Should Implement Robust Comprehensive Online Publicly Available State-by-State Produced Water Tracking Systems

Flowback and produced water may undergo various waste handling processes before the wastewater reaches its final destination for reuse or disposal. Produced water may be temporarily stored in surface impoundments, sent to processing or transfer facilities, or sent to treatment facilities prior to surface discharge. Produced water also may be re-injected directly on site to enhance hydrocarbon production or it may be sent for reuse at other neighboring or distant well pads. The variety of waste handling methods and potential combinations of these methods present different pathways for produced water to enter the environment and potentially come in contact with human populations and ecological receptors. Therefore, it is necessary to understand how waste is handled and how it travels from where it is generated to its final destination so that researchers and regulatory agencies can adequately evaluate spatially-explicit impacts to water and environmental quality and potential hazards, risks and impacts to human health.

Among oil and gas states, Pennsylvania provides the most comprehensive, publicly available dataset of oil and gas waste generation and waste handling. However, a recent investigation of available oil and gas waste data reported to the Pennsylvania Department of Environmental Protection from 1991 through 2017 revealed that existing reporting lacks sufficient detail to adequately track the final destination of liquid waste. Hill et al. (2019) found that 43% of the liquid waste volume across all years of data lacked a distinct spatially listed intermediary or final waste endpoint. Pennsylvania Chapter 78a regulations passed in 2016 required operators to report specific facility or well site information where the waste was managed for unconventional waste, but this regulation does not apply to conventional waste. In 2017, the new regulation resulted in 99% and 45% of unconventional and conventional liquid waste, respectively reported with an intermediary location or final spatial endpoint (Hill et al., 2019).

While spatial information on oil and gas waste storage and disposal has largely improved over time, waste is often reported at an intermediary stage as waste is stored or transferred rather than reporting the final destination of waste. Across all years of data, approximately one-third of all liquid waste did not have a reported final destination, either because the destination was not provided, or more commonly because the destination provided was an intermediary site such as a surface impoundment, treatment plant, or processing facility. In 2017, 40.8% of the liquid waste volume generated in that year reported was associated with an intermediary location (Hill et al., 2019).

Furthermore, liquid and solid waste co-produced from oil and gas development in one state may not stay within the state. For example, between 1995 and 2017 a significant proportion of liquid waste generated in Pennsylvania had been disposed in the neighboring states of Ohio (13.8%),

West Virginia (0.7%), and New York (0.1%). In some cases, waste produced in Pennsylvania had been reported as disposed at facilities as far as Idaho and Utah (Hill et al., 2019).

California recently adopted more detailed reporting and produced water from oil and gas operations via Senate Bill 1281 (SB 1281) which included additional information about water disposition, as well as the inclusion of treatment categories. However, data collected from SB 1281 reporting still lacks spatial resolution to determine precisely where waste ends up.

To evaluate the ongoing impact or potential impact of the discharge of produced water to surface water, a geographic information system (GIS) is necessary to determine locations of direct and indirect discharge locations, flow rates of effluent and the receiving water body, level of treatment prior to discharge, and the chemical composition of produced water and receiving water body. This would enable investigators and regulators to prioritize the evaluation of locations of ongoing impact or potential impact to surface water and sediment. If surface water and sediment sampling indicate impact or risk of impact to ecological or human receptors, information provided by a GIS would facilitate assignment of liability to oil and gas producers.

Due to exemption of produced water from Subtitle C of the Resource Conservation and Recovery Act (RCRA), there is no “cradle to grave” tracking of produced water in any state. Without a cradle-to-grave system in place to fully track waste from the time it is generated to the time it reaches its final disposal location, researchers and regulatory agencies cannot adequately evaluate spatially-explicit impacts or risk of impact to surface water and potential hazards to human and ecological receptors. Comprehensive robust tracking of produced water from generation to final endpoints is necessary to evaluate risks posed to human and ecological receptors from the discharge of produced water to surface water.

EPA does not have a comprehensive understanding of how many CWT facilities exist in the United States, where they are located, and how they are regulated (EPA 2018b). Hence, it is not currently possible to assess potential ongoing impact to surface water throughout the United States as a result of discharging produced water let alone the potential impact of increasing discharge of produced water to surface water. A prerequisite for any revisions on regulations for discharge of produced water to surface water should be a requirement for the development of a comprehensive robust online publicly accessible waste tracking system.

The Expanded “Beneficial” Use of Produced Water for Agriculture is not the Solution to Water Scarcity Issues

Finally, in the draft EPA report, EPA stated that individuals surveyed from state agencies and tribes generally supported increasing opportunities for management of produced water to provide additional water for agriculture (EPA 2019). However, the use of produced water for irrigation does not require a NPDES permit and is not regulated under the CWA (EPA 2019). Hence, discussion of the “beneficial” use of produced water for irrigation to support an argument for increased discharge of produced water to surface water in the draft EPA report is irrelevant.

As stated in the draft EPA report, the permitted use of produced water for irrigation of crops is limited and occurs primarily in California. In California, relatively low salinity produced water from only five oil fields (Deer Creek, Jasmin, Kern River, Kern Front, and Mount Poso) in Kern County is currently used for irrigation (CCST and LBNL 2015b). Currently, recycled produced water accounts for about 1% of irrigation water use in Kern County (Heberger and Donnelly 2015).

Based on data between 2000 and 2005 obtained from the U.S. Geological Survey, approximately 3.42 million acre-feet per year (AFY) of water was used for irrigation while only 168 thousand AFY was produced from oil and gas wells (Guerra et al. 2011) in California (1 acre-foot = 325,851 gallons). Even if all produced water was desalinated for use in agriculture, this would only account for 0.5% of state-wide demand. Using datasets for produced water generation and agricultural use for all western states (Guerra et al. 2011), if all produced water was desalinated, produced water would account for only 1.1% of water used for agriculture.

In the draft EPA report, individuals from industry acknowledged that unless produced water has total dissolved solids concentrations generally of less than a few thousand mg/L, treatment using membrane technology (e.g., reverse osmosis) or distillation would be necessary to make produced water fit for agricultural use (EPA 2019). These individuals stated further that the cost of such treatment is not currently competitive where other wastewater management options are available (EPA 2019). Hence, the use of produced water for agriculture is not the solution to water scarcity issues in the western United States.

Conclusion

The EPA has stated in its draft report released for public comment that it is considering increasing discharge options of produced water to surface water under the CWA. Based upon previous statements made by the Agency regarding concerns about the safety of discharging produced water to surface water and a growing body of information available in the peer-reviewed literature on this topic, increasing options for the increased discharge of produced water to surface water is unwarranted.

The 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 indeterminate. Complete disclosure of all chemicals used for all oil and gas development is necessary if the endpoint of produced water disposal can impact human or ecological receptors.

Chemical analysis performed at commercial laboratories using standard EPA 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. High levels of total dissolved solids and organic matter can cause matrix interference using standard EPA methods resulting in a negative bias in detection and quantification.

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 effectiveness of treatment and the risk posed by the discharge of produced water to surface water, 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 EPA 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 formidable objective. Expanding discharge options under the CWA magnifies this concern.

Compounding issues associated with the identification and quantification of compounds in produced water is the fact that little is known about the physiochemical, 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.

Field studies have indicated exceedance of regulated contaminant levels and impact to aquatic receptors and vegetation in riparian areas. Given that the discharge of produced water to surface water is already impacting aquatic receptors, the expansion of discharge opportunities can only worsen ongoing impact. Of considerable concern is that the commonly used effluent standard of 2.22 Bq/L or 60 pCi/L radium is causing accumulation of ^{226}Ra in sediment well beyond acceptable regulatory levels. Reduction of ^{226}Ra to background levels will require thousands of years.

Another concern is the generation of carcinogenic DBPs at drinking water intakes downstream of produced water discharge points due to elevated levels of bromide and ammonium. Drinking water plants downstream of produced water effluent have already noted a shift in bromated

DBPs. Increasing surface water discharge opportunities will increase human exposure to carcinogenic DBPs.

At present, treatment of produced water is often limited to oil-water separation, or in more saline produced water, chemical precipitation. ELGs do not contain limitations and associated treatment requirements for many compounds known to be present in produced water. Also, some discharge facilities operate with expired permits or no permits at all. It is difficult to justify expansion of discharge to surface water when current discharge is poorly regulated.

The treatment of produced water generates significant residual waste, some of which is highly radioactive and will remain so for thousands of years. Robust interstate tracking of this waste should be an urgent priority for EPA and should precede any efforts to increase this waste volume by facilitating greater discharge to surface water.

Finally, to evaluate the ongoing impact of the discharge of produced water to surface water, individual states must create geographical information systems to track endpoints of produced water disposal. These systems would also facilitate assignment of liability to oil and gas operators for impact to surface water and sediment. At present, due to exemption of produced water from Subtitle C of RCRA, there is no “cradle to grave” tracking of produced water in any state.

References

Abdullah K., Malloy T., Stenstrom M.K., Suffet I.H. 2017. Toxicity of acidization fluids used in California oil exploration. *Toxicology & Environmental Chemistry* 99, 78-94.

Agency for Toxic Substances and Disease Registry (ASTDR). Radium. July 1999. Available at <https://www.atsdr.cdc.gov/toxfaqs/tfacts144.pdf>

Akob D.M., Mumford A.C., Orem W., Engle M.A., Klinges J.G., Kent D.B., Cozzarelli I.M. 2016. Wastewater disposal from unconventional oil and gas development degrades stream quality at a West Virginia Injection Facility. *Environmental Science & Technology* 50, 5517-5525.

ALL Consulting. 2003. Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives. Prepared For: Ground Water Protection Research Foundation, U.S. Department of Energy National Petroleum Technology Office, Bureau of Land Management

Butkovskiy A., Bruning H., Kools S.A.E., Huub H.M., Rijnaarts H.H.M., Van Wezel A.P. 2017. Organic pollutants in shale gas flowback and produced waters: Identification, potential ecological impact, and implications for treatment strategies. *Environmental Science & Technology* 51, 4740–4754.

Boelter A.M., Lamming F.N., Farag A.M., Bergman H.L. 1992. Environmental effects of saline oil-field discharge on surface waters. *Environmental Toxicology & Chemistry* 11, 1187-1195.

California Council on Science & Technology, and Lawrence Berkeley National Laboratory (CCST and LBNL). 2015. An Independent Scientific Assessment of Well Stimulation in California, Volume II: Potential Environmental Impacts of Hydraulic Fracturing and Acid Stimulation. Vol. II. Sacramento, California. Available at: http://ccst.us/projects/hydraulic_fracturing_public/SB4.php.

DeArmond P.D., DiGoregorio A.L. 2013a. Rapid liquid chromatography–tandem mass spectrometry-based method for the analysis of alcohol ethoxylates and alkylphenol ethoxylates in environmental samples. *Journal of Chromatography A* 1305, 154-163.

DeArmond P.D., DiGoregorio A.L. 2013b. Characterization of liquid chromatography-tandem mass spectrometry method for the determination of acrylamide in complex environmental samples. *Analytical and Bioanalytical Chemistry* 405, 4159–4166.

Domestic Energy Producers Alliance. 2018. Comments of the Domestic Energy Producers Alliance for the Public Meeting on EPA’s Study of Oil and Gas Extraction Wastewater Management – Docket ID No. EPA-HQ-OW-2018-0618. Available at <https://www.regulations.gov/docketBrowser?rpp=25&so=DESC&sb=commentDueDate&po=0&dct=PS&D=EPA-HQ-OW-2018-0618>

Elsner M., Hoelzer K. 2016. Quantitative survey and structural classification of hydraulic fracturing chemicals reported in unconventional gas production. *Environmental Science & Technology* 50, 3290-3314.

Esmoil B.J., Anderson S.H. 1995. Wildlife mortality associated with oil pits in Wyoming. *Prairie Naturalist* 27(2), 81-88

Federal Register 88126, Vol. 81, No. 235 Effluent Limitations Guidelines and Standards for the Oil and Gas Extraction Point Source Category - Implementation Date Extension. Available at <https://www.govinfo.gov/content/pkg/FR-2016-12-07/pdf/2016-29338.pdf>

Ferrar K.J., Michanowicz D.R., Christen C.L., Mulcahy N., Malone S.L., Sharma R.K. 2013. Assessment of effluent contaminants from three facilities discharging Marcellus shale wastewater to surface waters in Pennsylvania. *Environmental Science & Technology* 47(7), 3472-3481.

Ferrer I., Furlong E.T. 2001. Identification of alkyl dimethylbenzylammonium surfactants in water samples by solid-phase extraction followed by ion trap LC/MS and LC/MS/MS. *Environmental Science & Technology* 35(12), 2583-2588.

Ferrer I., Furlong E.T. 2002. Accelerated solvent extraction followed by on-line solid-phase extraction coupled to ion trap LC/MS/MS for analysis of benzalkonium chloride in sediment samples. *Analytical Chemistry* 74(6), 1275-1280.

Ferrer I., Thurman, E.M. 2015. Analysis of hydraulic fracturing additives by LC/Q-TOF-MS. *Analytical and Bioanalytical Chemistry* 407(21), 6417-6428.

Getzinger G.J., O'Connor M.P., Hoelzer K., Drollette B.D., Karatum O., Deshusses M.A., Ferguson P.L., Elsner M., Plata D.L. 2015. Natural gas residual fluids: Sources, endpoints, and organic chemical composition after centralized waste treatment in Pennsylvania. *Environmental Science & Technology* 49(14), 8347-8355.

Gromatzky L G. 2019. Expanded Produced Water Discharge Options – On the Horizon? The Nickel Report – Trends and Development in Environmental Law. Available at <https://www.huntonnickelreportblog.com/2019/05/expanded-produced-water-discharge-options-on-the-horizon/>

Groundwater Protection Council (GWPC) 2014. State Oil & Gas regulations Designed to Protect Water Resources. Available at <http://www.gwpc.org/state-oil-gas-regulations-designed-protect-water-resources-2014-edition>

Guerra K., Dahm K., Dundorf S. 2011. Oil and Gas Produced Water Management and Beneficial Use in the Western United States. U.S. Department of the Interior, Bureau of Reclamation, Technical Service Center, Water and Environmental Resources Division, Water Treatment Engineering Research Group, Denver, Colorado. Available at <https://www.usbr.gov/research/dwpr/reportpdfs/report157.pdf>

He Y., Folkerts E. J., Zhang Y., Martin J. W., Alessi D. S., Goss G. G. 2017. Effects on Biotransformation, Oxidative Stress, and Endocrine Disruption in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Hydraulic Fracturing Flowback and Produced Water. *Environmental Science & Technology* 51(2), 940–947.

Heberger M, Donnelly K. 2015. Oil, Food, and Water: Challenges and Opportunities for California Agriculture. Pacific Institute, Oakland, CA, December 2015. Available at: <https://pacinst.org/publication/oil-food-and-water-challenges-and-opportunities-for-california-agriculture/>

Hill L.L., Czolowski E.D., DiGiulio D.C., Shonkoff S.B.C. 2019. Temporal and spatial trends of conventional and unconventional oil and gas waste management in Pennsylvania, 1991–2017. *Science of the Total Environment* 674, 623-636.

Hladik M.L., Focazio M.J., Engle M. 2014. Discharges of produced waters from oil and gas extraction via wastewater treatment plants are sources of disinfection by-products to receiving streams. *Science of the Total Environment* 466-467,1085-1093.

Hoelzer K., Sumner A. J., Karatum O., Nelson R. K., Drollette B. D., O'Connor M. P., D'Ambro E. L., Getzinger G. J., Ferguson P. L., Reddy C. M., Elsner M., Plata, D. L. 2016. Indications of transformation products from hydraulic fracturing additives in shale-gas wastewater. *Environmental Science & Technology* 50, 8035-8048.

International Atomic Energy Agency, The Environmental Behaviour of Radium, revised edition, Vienna, 2014.

- Kahrilas G. A., Blotevogel J., Stewart P. S., Borch T. 2015. Biocides in Hydraulic Fracturing Fluids: A Critical Review of Their Usage, Mobility, Degradation, and Toxicity. *Environmental Science & Technology* 49(1), 16–32.
- Kassotis C.D., Iwanowicz L.R., Akob D.M., Cozzarelli I.M., Mumford A.C., Orem W.H., Nagel S.C. 2016. Endocrine disrupting activities of surface water associated with a West Virginia oil and gas industry wastewater disposal site. *Science of the Total Environment* 557-558, 901-910.
- Kassotis C. D., Bromfield J. J., Klemp K. C., Meng C.-X., Wolfe A., Zoeller R. T., Balise V.D., Isiguzo C. J., Tillitt D.E., Nagel, S. C. 2016. Adverse Reproductive and Developmental Health Outcomes Following Prenatal Exposure to a Hydraulic Fracturing Chemical Mixture in Female C57Bl/6 Mice. *Endocrinology*, en.2016-1242. <https://doi.org/10.1210/en.2016-1242>
- Kassotis, C. D., Nagel, S. C., & Stapleton, H. M. 2018. Unconventional oil and gas chemicals and wastewater-impacted water samples promote adipogenesis via PPAR γ -dependent and independent mechanisms in 3T3-L1 cells. *Science of The Total Environment*. <https://doi.org/10.1016/j.scitotenv.2018.05.030>
- Lee M. 2018. Oil patch states want authority for wastewater solutions. E & E News. Available at <https://www.eenews.net/stories/1060110201>
- Lester Y.; Ferrer I., Thurman E.M., Sitterley K.A., Korak J.A., Aiken G., Linden K.G. 2015. Characterization of hydraulic fracturing flowback water in Colorado: Implication for water treatment. *Science of the Total Environment* 512-513, 637-644.
- Liberatore H. K., Plewa M. J., Wagner E. D., VanBriesen J. M., Burnett D. B., Cizmas L. H., Richardson S. D. 2017. Identification and Comparative Mammalian Cell Cytotoxicity of New Iodo-Phenolic Disinfection Byproducts in Chloraminated Oil and Gas Wastewaters. *Environmental Science & Technology Letters* 4(11), 475–480.
- Luek J.L., Schmitt-Kopplin P., Mouser P.J., Petty W.T., Richardson S.D., Gonsior M. 2017. Halogenated organic compounds identified in hydraulic fracturing wastewaters using ultrahigh resolution mass spectrometry. *Environmental Science & Technology* DOI: 10.1021/acs.est.6b06213.
- Luh J., Mariñas B. J. 2014. Bromide ion effect on N-nitrosodimethylamine formation by monochloramine. *Environmental Science & Technology* 46, 5085–5092.
- McDevitt B., McLaughlin M., Cravotta III C.A., Ajemigbitse M.A., Van Sice K.J., Blotevogel J., Borch T., Warner N.R. 2018. Emerging investigator series: radium accumulation in carbonate river sediments at oil and gas produced water discharges: implications for beneficial use as disposal management. *Environmental Science Processes & Impacts*. DOI: 10.1039/c8em00336j
- Nell M., Helbling D.E. 2018. Exploring matrix effects and quantifying organic additives in hydraulic fracturing associated fluids using liquid chromatography. *Environmental Sciences: Processes & Impacts* 21, 195-205.

Nelson A.W., May D., Knight A.W., Eitrheim E.S., Mehrhoff M. Shannon R., Litman R., Schultz M.K. 2014. Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale. *Environmental Science & Technology Letters* 1, 204-208.

Orem W., Varonka M., Crosby L., Haase K., Loftin K., Hladik M., Akob D.M., Tatu C., Mumford A., Jaeschke J., Bates A., Schell T., Cozzarelli I. 2017. Organic geochemistry and toxicology of a stream impacted by unconventional oil and gas wastewater disposal operations. *Applied Geochemistry* 80, 155-167.

Ouyang B., Akob D.M., D. Dunlap D., Renock D. 2017. Microbially mediated barite dissolution in anoxic brines. *Applied Geochemistry* 76, 51–59.

Parker K.M., Zeng T., Harkness J., Vengosh A., Mitch W.A. 2014. Enhanced formation of disinfection byproducts in shale gas wastewater-impacted drinking water supplies. *Environmental Science & Technology* 48, 11161-11169.

Phillips E.J.P., Landa E.R., Kraemer T., Zielinski R. 2001. Sulfate-reducing bacteria release barium and radium from naturally occurring radioactive material in oil-field barite. *Geomicrobiology Journal* 18, 167–182.

Plewa M.J., Wagner E.D., Jazierska P., Richardson S.D., Chen P.H., McKague A.B. 2004. Halonitromethane drinking water disinfection byproducts: chemical characterization and mammalian cell cytotoxicity and genotoxicity. *Environmental Science & Technology* 38, 62-68.

Ramirez P. 2002. Oil Field Produced Water into Wetlands in Wyoming. U.S. Fish & Wildlife Service, Ecological Services, Wyoming Field Office, Cheyenne, Wyoming. Available at: <https://www.fws.gov/mountain-prairie/contaminants/papers/r6718c02.pdf>

Regulations.gov 2018. Docket on Study of Oil and Gas Extraction Wastewater Management Under the Clean Water Act Available at: <https://www.regulations.gov/docketBrowser?rpp=25&so=DESC&sb=commentDueDate&po=0&dct=PS&D=EPA-HQ-OW-2018-0618>

Renock D., Landis J.D., Sharma M. 2016. Reductive weathering of black shale and release of barium during hydraulic fracturing. *Applied Geochemistry* 65, 73–86.

Richardson S.D., Plewa M. J., Wagner E. D., Schoeny R., DeMarini D. M. 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutagen Research* 636, 178–242.

Richardson S.D., Fasano F., Ellington J.J., Crumley F.G., Buettner K.M., Evans J.J., Blount B.C., Silva L.K., Waite T.J., Luther G.W. 2008. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environmental Science & Technology* 42(22), 8330-8338.

Robert J., McGuire C. C., Kim F., Nagel S. C., Price S. J., Lawrence B. P., De Jesús Andino F. 2018. Water contaminants associated with unconventional oil and gas extraction cause immunotoxicity to amphibian tadpoles. *Toxicological Sciences*. <https://doi.org/10.1093/toxsci/kfy179>

Rogers J.D., Burke T.L., Osborn S.G., Ryan J.N. 2015. A framework for identifying organic compounds of concern in hydraulic fracturing fluids based on their mobility and persistence in groundwater. *Environmental Science & Technology* 2, 158-164.

Rosenblum J., Thurman E.M., Ferrer I., Aiken G., Linden K.G. 2017. Organic chemical characterization and mass balance of a hydraulically fractured well: From fracturing fluid to produced water over 405 Days. *Environmental Science & Technology* 51 (23), 14006–15.

Rowan E.L., Engle M.A., Kraemer T.F., Schroeder K.T., Hammack R.W., Doughten M.W., 2015. Geochemical and isotopic evolution of water produced from middle Devonian Marcellus shale gas wells, Appalachian basin, Pennsylvania. *American Association of Petroleum Geologists Bulletin* 99, 181–206.

Saunders N. 2019 Trump’s EPA may weaken restrictions on disposal of oilfield wastewater — here’s what you need to know. Blog published February 26, 2019 available at <http://blogs.edf.org/energyexchange/author/nsaunders/>

Shah A. D., Krasner S. W., Lee C. F. T., von Gunten U., Mitch W. A. 2012a. Trade-offs in disinfection byproduct formation associated with precursor preoxidation for control of N-nitrosodimethylamine formation. *Environmental Science & Technology* 46, 4809–4818.

Shah A. D., Mitch W. A. 2012. Halonitroalkanes, halonitriles, haloamides and N-nitrosamines: A critical review of nitrogenous disinfection byproduct (N-DBP) formation pathways. *Environmental Science & Technology* 46, 119–131.

Shonkoff S.B.C., Maddalena R.L., Hays J., Stringfellow W., Wettstein Z.S., Harrison R., Sandelin W., McKone T.E. 2015. *Potential Impacts of Well Stimulation on Human Health in California*. In: *An Independent Scientific Assessment of Well Stimulation in California*. California Council on Science and Technology, Sacramento, CA. Available at: <http://ccst.us/publications/2015/vol-II-chapter-6.pdf>

Shonkoff S.B.C., Domen J.K., Stringfellow W.T. 2016. *Hazard Assessment of Chemical Additives Used in Oil Fields that Reuse Produced Water for Agricultural Irrigation, Livestock Watering, and Groundwater Recharge in The San Joaquin Valley of California: Preliminary Results*. Technical Report. PSE Healthy Energy, Inc. Oakland, CA. September 2016. Available at: http://psehealthyenergy.org/data/Preliminary_Results_13267_Disclosures_FINAL.pdf

Smith K.P. 1992. An Overview of Naturally Occurring Radioactive Materials (NORM) in the Petroleum Industry. Argonne National Laboratory, ANL/EAIS-7, December 1992. Available at <https://www.osti.gov/servlets/purl/6594778>

Stringfellow W.T., Domen J.K., Camarillo M.K., Sandelin W.L., Borglin S. 2014. Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing. *Journal of Hazardous Materials* 275, 34-54.

Stringfellow W.T., Camarillo M.K., Domen J.K., Sandelin W.L., Varadharajan C., Jordan P.D., Reagan M.T., Cooley H., Heberger M.G., Birkholzer J.T. 2017a. Identifying chemicals of concern in hydraulic fracturing fluids used for oil production. *Environmental Pollution* 220, 413-420.

Stringfellow W.T., Camarillo M.K., Domen J.K., Shonkoff S.B.C. 2017b. Comparison of chemical-use between hydraulic fracturing, acidizing, and routine oil and gas development. *PLoS ONE* 12(4): e0175344. <https://doi.org/10.1371/journal>.

Tasker T.L., Burgos W.D., Piotrowski P., Castillo-Meza L., Blewett T.A., Ganow K.B., Stallworth K.B.A., Delompre P.L.M., Goss G.G., Fowler L.B., vanden Heuvel J.P., Dorman F. Warner, N. R. 2018. Environmental and Human Health Impacts of Spreading Oil and Gas Wastewater on Roads. *Environmental Science & Technology*. <https://doi.org/10.1021/acs.est.8b00716>

Thurman M.E., Ferrer I., Blotevogel J., Borch T. 2014. Analysis of hydraulic fracturing flowback and produced waters using accurate mass: Identification of ethoxylated surfactants. *Analytical Chemistry* 2014, 86, 9653-9661.

Thurman M.E., Ferrer I., Rosenblum J., Linden K., Ryan J.N. 2017. Identification of polypropylene glycols and polyethylene glycol carboxylates in flowback and produced water from hydraulic fracturing. *Journal of Hazardous Materials* 323, 11-17.

United States Environmental Protection Agency (EPA) 1995. Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings (40 CFR Part 192). Available at <https://www.epa.gov/radiation/health-and-environmental-protection-standards-uranium-and-thorium-mill-tailings-40-cfr>

U.S. Environmental Protection Agency (EPA) 2010. Coalbed Methane Extraction: Detailed Study Report, EPA-820-R-10-022, Office of Water (4303T). Washington, DC 20460

United States Environmental Protection Agency (EPA) 2015. Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0. EPA/601/R-14/003. Available at https://www.epa.gov/sites/production/files/2015-03/documents/fracfocus_analysis_report_and_appendices_final_032015_508_0.pdf

United States Environmental Protection Agency (EPA) 2016. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States, EPA-600-R-16-236fa, Office of Research and Development, Washington, D.C. Available at <https://www.epa.gov/hfstudy>

United States Environmental Protection Agency (EPA) 2018a. Public Meeting EPA Oil and Gas Extraction Study Effluent Guidelines Program October 9, 2018 Washington, DC. Available at: https://www.epa.gov/sites/production/files/2018-10/documents/epa_oil-gas-study_public-meeting_10-09-2018.pdf

United States Environmental Protection Agency (EPA) 2018b. Detailed Study of the Centralized Waste Treatment Point Source Category for Facilities Managing Oil and Gas Extraction Wastes, EPA-821-R-18-004, Engineering and Analysis Division, Office of Water, May 2018.

United States Environmental Protection Agency (EPA) 2019a. Study of Oil and Gas Extraction Wastewater Management Under the Clean Water Act, EPA-821-R19-001, Office of Water, Washington D.C., May 2019. Available at <https://www.epa.gov/eg/study-oil-and-gas-extraction-wastewater-management>

United States Environmental Protection Agency (EPA) 2019b. Whole Effluent Toxicity Methods. Available at: <https://www.epa.gov/cwa-methods/whole-effluent-toxicity-methods>

United States Nuclear Regulatory Commission, Appendix B to Part 20. 2017. Annual Limits on Intake (ALIs) and Derived Air Concentrations (DACs) of Radionuclides for Occupational Exposure; Effluent Concentrations, Concentrations for Release to Sewerage.

Warner N.R., Christie C.A., Jackson R.B., Vengosh A. 2013. Impacts of shale gas wastewater disposal on water quality in western Pennsylvania. *Environmental Science & Technology* 47, 11849-11857.

Wei X., Wang S., Zheng W., Wang X., Liu X., Jiang S., Pi J., Zheng Y., He G., Qu W. 2013. Drinking water disinfection byproduct iodoacetic acid induces tumorigenic transformation of NIH3T3 cells. *Environmental Science & Technology* 47, 5913–5920.

Yao Y., Chen T., Shen S. S., Niu Y., DesMarais T.L., Linn R., Saunders E., Fan Z., Liyo P., Kluz T., Chen L-C., Wu Z., Costa M. 2015. Malignant human cell transformation of Marcellus Shale gas drilling flow back water. *Toxicology and Applied Pharmacology* 288, 121–130. <https://doi.org/10.1016/j.taap.2015.07.011>.

Yost E. E., Stanek J., DeWoskin R.S., Burgoon L.D. 2016. Overview of chronic oral toxicity values for chemicals present in hydraulic fracturing fluids, flowback, and produced waters. *Environmental Science & Technology* 50, 4788-4797.