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TOC/Conductivity: Surrogate Measurements Potentially Guiding Greater Utilization of Treated Produced Water

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Abstract: Hydraulic fracturing utilizes pressurized liquid typically consisting of water, proppants, and a multitude of chemical additives, in order to fracture petroliferous strata to extract natural gas and oil. In this process, a vast amount of wastewater is produced. This water is heavily contaminated, which renders it unusable outside of direct reuse, without extensive treatment being performed. Typically, various sophisticated analytical techniques are involved in the characterization of both waste and treated waters, increasing the cost and the complexity of the management efforts. The article discusses the constituents found in oilfield wastewater, the methods used to identify and quantify these constituents, and the present management methods. Additionally, we introduce total organic carbon and conductivity analyses as surrogate measurements of overall water quality. Total organic carbon and conductivity are established bulk measurements, which can be used to facilitate rapid decisions regarding the treatment and greater utilization of flowback and produced oilfield wastes. The application of the proposed surrogates could be used to streamline the current myriad of complex and expensive measurements. This would improve operational efficiency with respect to wastewater management in the energy sector.

Keywords: produced water; flowback water; water treatment; untargeted environmental analysis

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1. The Composition and Analysis of Flowback and Produced Waters

Unconventional oil and gas development (UD) is the process of extracting petroleum hydrocarbons from impermeable subsurface strata, such as shale, using large volumes of water, proppants, and chemical additives. The stimulation of UD production wells yields two distinct waste streams: flowback water (FBW), which is representative of the composition of the stimulation fluid (i.e., source water and hydraulic fracturing additives), and produced water (PW), which is characteristic of the biogeochemical composition of the petroliferous strata of interest [1,2]. Collectively, these two waste streams are referred to as flowback and produced water (FP) [3], the management of which requires significant financial and operational resources to accommodate annual productions in excess of the 1700 ($\times 10^6$) barrels in the Permian Basin alone [4].

From an analytical perspective, FP is one of the most complex mixtures known to man. It consists of a wide array of biogeochemical constituents, which can vary greatly depending on the components used during hydraulic fracturing and the composition of the subsurface geology [5]. Elevated levels of sodium and chloride ions are distinctive characteristics of these brines. Chloride concentrations in FP derived from the Permian Basin region of western Texas typically oscillate around 15% w/v, whereas Na concentrations fluctuate around 7% w/v. FP can also contain naturally occurring radioactive materials

(NORM) [6]. Several studies have reported significant concentrations of radium isotopes in PW [7,8] as well as trace levels of radioactive cesium, lead, strontium, thorium, and uranium [9]. Other prominent inorganic constituents include iron, magnesium, strontium, and calcium [8,10–12].

The organic constituents found in FP can be classified into three major categories: aliphatics, aromatics, and drilling additives [13]. Aliphatics include small chain hydrocarbons (dissolved oil components), alkylethoxylates [14], long chain fatty acids, and heterocyclic compounds [15]. Examples of aromatics found in PW include polycyclic aromatic hydrocarbons (PAH's), xylenes, phenols, and alkyl benzenes [14–17]. Chemical additives can be further divided into three major types: alcohols, biocides, and surfactants. Prominent alcohols include ethanol, isopropanol, methanol and propargyl alcohol [18], as well as phenols, ethylene glycol, other ethoxylated alcohols, and tertbutyl alcohol [19]. Biocides are added in hydraulic fracturing fluid to control the proliferation of bacteria. Some of the commonly used biocides include glutaraldehyde, quaternary ammonium compounds (QACs), sodium hypochlorite (and other oxidizing agents), and tetrakishydroxymethylprosphonium sulfate (THPS). The biodegradability of these compounds varies from rapidly biodegradable (e.g., THPS) to environmentally persistent (e.g., QACs) [15,18–21]. Surfactants control viscosity of fracturing liquids and increase fluid recovery. As many as 84 examples of these have been found in hydraulic fracturing fluids [21], including alcohol ethoxylates (AEOs), alkylphenol ethoxylates (APEOs), ethoxylated alcohols and phenols, cocamide compounds, sodium lauryl sulfate, and dimethyl dihydrogenated tallow ammonium chloride (DHTDMA) [18–20]. Additionally, a wide range of other unknown volatile or semi-volatile compounds can be present in FP [22,23]. The complexity of FP provides a tremendous impetus for the continued development of novel analytical methods to better understand the full breadth of organic constituents.

The geochemical richness of FP can provide an optimal environment for the proliferation of a vast range of microorganisms. These vary from obligate aerobes to obligate anaerobes, and include sulfate-reducing bacteria (SRB), iron-oxidizing bacteria (IRB), acid-producing bacteria (APB), and extremophiles. The presence of SRB (e.g., desulfomicrobium, desulfovibrio, desulfohalubium, desulfobacter) may lead to souring of natural gas, whereas IRB (e.g., desulfuromusa, pelobacter, malonomonas, desulfu-romonas) can cause corrosion in metal infrastructure [24,25]. APB (e.g., halanaerobium) generate metabolites, which can affect the integrity of grout and the casing of wells [26]. Extremophiles can also persist in FP. These microorganisms can withstand extreme water quality conditions like pH, temperature, and salinity, and are particularly difficult to neutralize with biocides due to changes in their membrane structure that make them relatively impermeable [23].

Numerous analytical techniques are required to comprehensively characterize the chemical composition of FP [23,27]. For example, methods used to detect and quantify the presence of volatile and semi-volatile organic compounds include gas chromatography coupled to mass spectrometry (GC-MS). Non-volatile constituents like surfactants can be measured using liquid chromatography-mass spectrometry (LC-MS). Additionally, the analysis of metal and non-metal ions is generally per-formed via inductively coupled plasma-optical emission spectrometry (ICP-OES) and/or inductively coupled plasma-mass spectrometry (ICP-MS). The characterization of major ions (i.e., chloride, sulfate, sulfide, fluoride, bromide, and ammonia) is performed primarily using ion chromatography (IC). Additional methods for the characterization and quantitation of microbial constituents include aerobic and anaerobic plate count (i.e., selective, and non-selective media), Gram-staining, microscopy, and molecular methods. Common molecular methods include polymerase chain reaction (PCR) and DNA sequencing. Matrix assisted laser desorption ionization-time of flight-mass spectrometry (MALDI-TOF-MS) is a relatively recent innovation that facilitates the rapid identification of microorganisms compared to traditional methods [28]. The use of these analytical techniques in concert provide considerable insight into the complex composition of FP.

Unfortunately, while being comprehensive, the aforementioned analyses are expensive and time-consuming; they cost hundreds to thousands of dollars per sample at a commercial testing laboratory and requiring multiple weeks for processing. On the contrary, the analysis of bulk water quality parameters, such as total dissolved solids (TDS), total suspended solids (TSS), turbidity, organic and inorganic carbon content (TOC and IC, respectively), pH and oxidation reduction potential (ORP), can be performed in situ by individuals with limited technical training using multiparametric sensors, titration, and gravimetric methods [23,28]. As will be discussed in this perspective, the use of these bulk surrogate measurements can yield considerable information about overall water quality. In particular, TOC/conductivity provide a cumulative evaluation of organic and inorganic constituents, respectively (Figure 1). When coupled with toxicological measurements (acute and chronic), TOC/conductivity measurements can provide valuable insight on the suitability of treated FPs for various terminal applications (direct reuse vs. beneficial reuse), thus potentially allowing operators to overcome the regulatory hurdles that currently preclude greater utilization of treated FP.

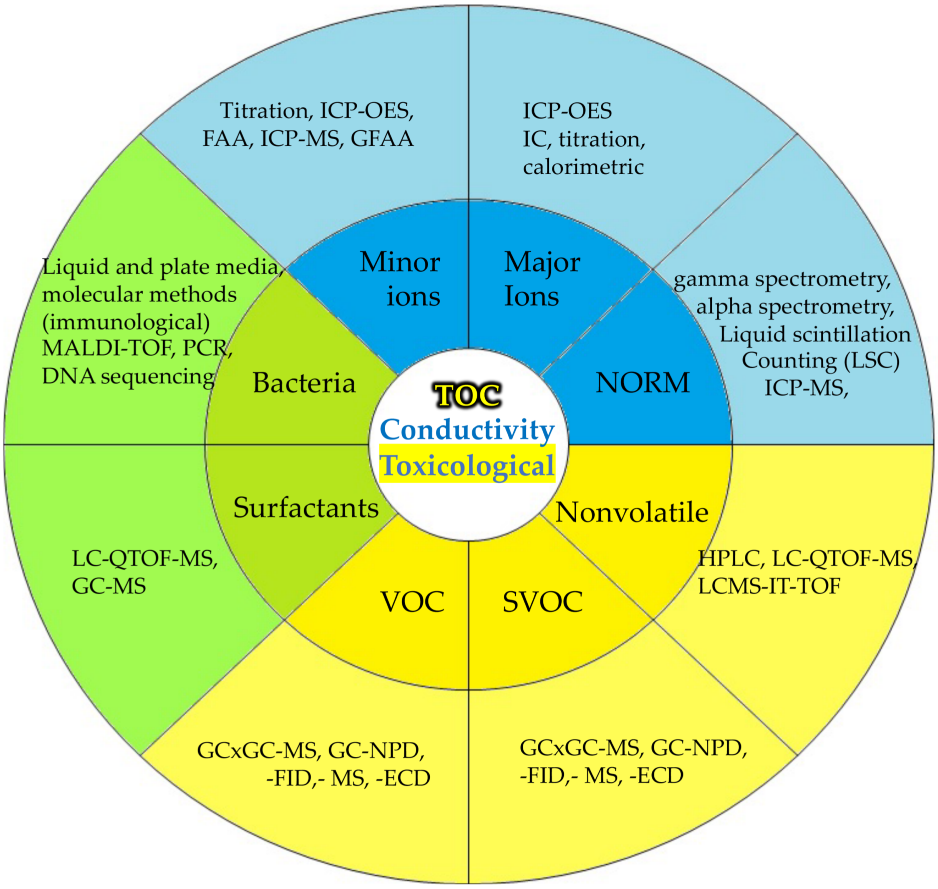

Figure 1. Schematic of the different classes of water quality constituents found in FP and the respective analytical techniques that are used for analyte detection and quantitation. The text for the two surrogate measurements TOC and conductivity listed in the center are color coded for the constituent classes of which they are representative. Toxicological analyses can be used in conjunction with TOC/conductivity measurements to cover potential signal from NORM and/or influence from volatile and semi-volatile compounds that would be detected by untargeted analyses. Adjusted with expressed written consent from Liden et al [27].

2. Current Management of FP

Traditionally, large volumes of FP are managed through disposal into the subsurface using saltwater disposal wells (SWDs). This process consists of transporting the FP, via trucking or pipelines, to designated sites where the fluid is pumped thousands of feet below the surface and sequestered into deep geologic formations. However, this practice comes with a series of environmental concerns. For example, spills during the transport of FP to disposal sites can lead to groundwater and surface water contamination. A recent study modeled different spillage scenarios with varying soil types, spill intensities, and depth of ground water; the study concluded that benzene and toluene (toxicity inducing compounds) are the primary contaminants of concern [29]. Similarly, a 2019 study reported an increase in bromide, radium, strontium, lithium, and boron downstream from a spill site in comparison to upstream, which translated into a reduction in the growth of fish and the survival of mussels [30]. Another significant concern associated with the subsurface disposal of FP through SWDs is the increased occurrence of seismic events in shale energy basins. Induced seismicity is a risk when injection is performed into deep bedrock formations as it may lubricate pre-existing geological faults and provoke fault slips [31]. Furthermore, subsurface injection has a particular association with earthquakes when actuating critically stressed faults to failures by increasing pore pressure [32]. In recent years, seismicity rates have increased by 12-fold since 2008 in the Permian Basin of Western Texas [33]. Moreover, documented cases of induced earthquakes have been observed in Canada, the United Kingdom, and China, with events of up to 5.7 on the Richter scale [34]. For these reasons, the state of New Mexico no longer grants permits for SWDs to operate in select formations as a preventative action to decrease the occurrence of seismicity in the area.

If the disposal of FP through SWDs is putting a stress on the peripheral environment and is a seemingly unsustainable form of waste management, there would need to be a robust alternative, such as treatment for direct reuse (hydraulic fracturing) or beneficial reuse (e.g., agricultural discharge), that could handle the large volumes of waste being produced in shale energy basins across the world. In the United States alone, the Marcellus, Eagle Ford, Bakken, and Permian Basin shale regions have reported annual FP volumes of 33.34, 220.80, 343.46 and 1663.21 million barrels (bbl), respectively [4]. These volumes are increasing, in conjunction with increased UD activity. For example, by 2017, the Permian Basin exhibited FP volumes that were approximately 20 times greater than in 2011 [4]. Taken as a whole, the potential treatment and reuse of FP for hydraulic fracturing would significantly reduce the reliance on freshwater and brackish water resources in shale energy regions, particularly in the Bakken and Permian Basins. Such practices would alleviate water stress in nearby communities by retaining large volumes of water in the water cycle. This paradigm shift would also simultaneously reduce the occurrence of injection-related induced seismicity. Additionally, if FP is treated to an appropriate standard, a growing number of applications are available, such as agricultural and surface water discharge, domestic usage, and aquifer recharge. Lastly, the treatment and valorization of FP using novel technologies could provide potential economic opportunities, such as the extraction of precious and semi-precious metals (i.e., cobalt, nickel, and lithium). The mining and extraction of precious metals found in FP represents a relatively unexplored opportunity for the energy sector.

3. The Impetus for Greater Utilization of Treated FP

Using the Permian Basin of Texas as an example, in 2017, a total of 1.66×10^9 bbl of PW were generated. In contrast, that same year, 1.32×10^9 bbl of water were utilized for HF operations [4]. If treated, the PW in the Permian region, in comparison to the amount required for production well stimulation, produces a surplus of 3.40×10^8 bbl, demonstrating that far more PW is being generated than can be utilized for direct reuse. This particular rate of PW generation substantiates the need to explore other outlets such as agricultural discharge or aquifer recharge (i.e., beneficial reuse).

Unfortunately, the regulatory framework to support these initiatives has not been established in Texas. Neither the Texas Railroad Commission (TRRC) nor the Texas Commission on Environmental Quality (TCEQ) has a permitting process in place to support beneficial reuse at scale. The creation of such framework might be shadowed by the perception that commercially available analytical tools are not yet suitable to comprehensively characterize all of the pertinent biogeochemical constituents that can persist in FP; hence, fit-for-purpose treatment for reuse is not an option [21]. To this particular point, commercial laboratories can screen for a suite of 60–100 volatile and semi-volatile organic compounds, a majority of which are moderately toxic and are targeted towards other industries outside of the energy sector. With regard to microorganisms, these laboratories may limit their screening to aerobic plate counts, in order to innumerate total bacteria; however, the composition and handling of FP makes it important to characterize the various species that can have deleterious effects on commodity composition and the structural integrity of surface infrastructure. Additionally, the wide range of metals present in FP are often at higher concentrations than typically managed by commercial laboratories, which generally only screen for a panel of 10 to 15 species at a time. Lastly, the implementation of untargeted analysis for the comprehensive study of potentially toxic organic species is time-consuming, expensive, and demands a level of technical expertise that is atypical of most laboratory technicians. Collectively, these factors substantiate the need to develop reliable surrogate measurements that can rapidly facilitate the characterization of treated FP. Particularly, quantifying conductivity and TOC values of treated FP can simplify the characterization process due to their low cost, easy operation, and reliability. These measurements can also help guide the technical standards for treated FP by creating the framework for better regulation of FP management in the shale energy sector.

Based on our historical measurements of raw and treated FPs (Figure 2), TOC values correlated with the number of detectable VOCs but did not reflect a similar relationship with the concentration of the BTEX class of compounds, the levels of which are generally a harbinger of hydrocarbon content [5]. Additionally, we have found that higher conductivity values correlated with increasing concentrations of chloride and prominent scaling (calcium, magnesium, barium, and strontium) ions found in FP from the Eagle Ford Basin in southern Texas [5]. These particular results illustrate the merits of collecting bulk measurements and suggests that TOC/conductivity could be effective surrogates for more complex analyses (Figure 1). Table 1 illustrates a hypothetical example of the relationship between TOC and conductivity values with parameters such as VOCs, bacteria, and toxicity. If a linear relationship exists between TOC/conductivity and acute and chronic toxicity, then this would greatly streamline decision-making regarding the terminal use of treated FPs and could guide the promulgation of new legislation and permitting processes that would better support beneficial use.

Table 1. Hypothetical examples of the possible relationships between TOC, conductivity, acute and chronic toxicities, and the presence of various organic and biological constituents found in FPs of varying water quality. OX: oxidizing agent, PF: particulate filtration, C: carbon filtration, RO: reverse osmosis, FD: flash distillation, CAV: cavitation, SD: solar distillation.

Source	Treatment	TOC (mg/L)	SPC (mS/cm)	# VOCs & SVOCs	# Untargeted Compounds	Bacteria (CFU/mL)	Acute Toxicity (1–10)	Chronic Toxicity (1–10)	Terminal Destination
Raw Permian	Raw	2300	140	85	21	5,000,000	10	9	Disposal
Partially Treated	OX, PF	100	130	15	5	2,000,000	5	8	Direct Reuse
Partially Treated	OX, PF, CF	25	110	5	3	1,500,000	4	5	Direct Reuse
Fully Treated	OX, PF, CF, RO	10	1	2	1	<1000	2	3	Agricultural Discharge
Fully Treated	OX, PF, CF, FD	5	0.5	1	0	<1000	2	2	Agricultural Discharge
Fully Treated	OX, CAV, SD	2.5	0.4	0	0	<1000	1	1	Agricultural Discharge

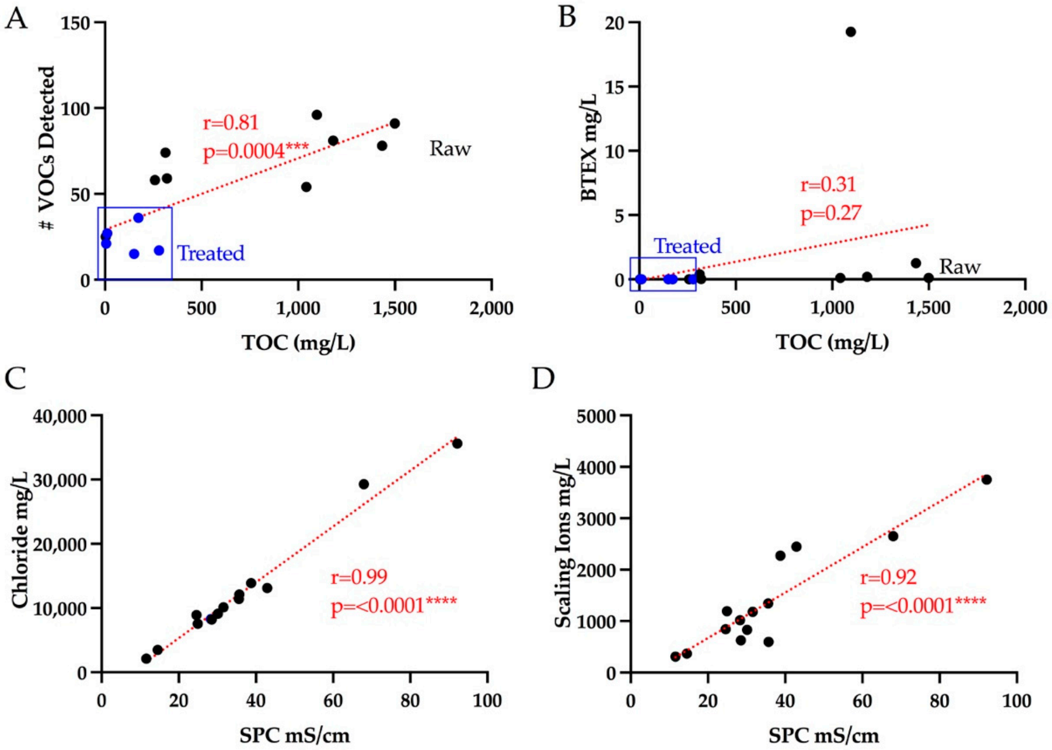

Figure 2. Correlative analysis of pertinent constituent classes and bulk measurements. (**A**) Total organic carbon (TOC) concentrations in relation to the number of volatile organic compounds (VOCs) detected in treated and untreated produced water from the Eagle Ford Shale region [5]. (**B**) TOC concentrations in relation to total BTEX concentrations (benzene, toluene, ethylbenzene, and m,p,o-xylenes). (**C**) Specific conductivity (SPC) measurements in relation to the concentrations of chloride ions. (**D**) SPC measurements in relation to the cumulative concentrations of the scaling ions barium, calcium, magnesium, and strontium. It is important to note that the efficacies of oxidation, particulate filtration, two different carbon medias, and UV treatment were evaluated in this study. Desalination modalities were not evaluated. *** and **** denote *p*-values less than 0.0005 and 0.0001, respectively.

3.1. FP Utilization and Permitting in New Mexico

Currently, NM is one of four states that does not currently have authority to act on behalf of the EPA. Efforts are currently being made, through the activities of the New Mexico Produced Water Consortium (NMPWC), for the New Mexico Environment Department (NMED) to gain this authorization, but it has not yet made a formal request. The authorization process is known to take at least two years. The New Mexico Groundwater Quality Bureau, through the NMED, is charged with the protection of groundwater quality in the state. It does issue permits for the discharge of water onto surface locations (so-called "land application") from industrial, agricultural, and mining sources. On 1 July 2019, New Mexico House Resolution (HR) 546, The Fluid Oil and Gas Waste Act, went into effect. HR 546 mandated state regulation of produced water and this spurred the creation of the NMPWC. The goal of the NMPWC is to provide collective feedback from industrial, governmental, environmental, and regulatory bodies regarding the best path forward for surface discharge of produced water in NM. This is an ongoing process. The NMPWC is very active, but there is currently no clear plan for how to receive permits for surface and water discharge of produced water in the state of New Mexico.

3.2. FP Utilization and Permitting in Texas

In Texas, the landscape is different; however, the potential for discharge of produced water is still in its infancy. In January 2021, the EPA authorized the TCEQ to issue TPDES permits for discharge into existing water bodies. Despite this development, to date, no new permits have been authorized for discharge of treated oilfield produced water. Each entity seeking discharge must provide specific details about their operations in order to obtain a permit. This includes information about the specific location of operation, the treatment design and process, and the influent water quality. Even if a relevant permit has yet to be issued, a path exists in Texas for the potential discharge of large volumes of treated produced water. Additional permitting would also be needed for any additional emissions or disposal associated with a treatment and discharge operation.

Land application (i.e., agricultural use) permits for treated produced water can be obtained from the TRRC, albeit none have been issued for the beneficial reuse of treated FP of any significant scale. Permitting would apply to a clearly defined surface location, with a specific surface area and clearly delineated minimum effluent quality specifications. The drawback of this approach is the strict limitation of the surface area over which discharge can occur, and this likely limits the overall volume of treated produced water that could be discharged in any single location.

A variety of information will need to be supplied to apply for a permit. This includes the expected discharge rate (flow rate) associated with the process. Influent and effluent constituent concentrations need to be measured to determine levels of organics, total dissolved/suspended solids (TDS and TSS), metals, naturally occurring radioactive material (NORM), and whole effluent toxicity (WET). A plan for disposal of any byproducts (e.g., a concentrated waste stream) from the treatment process must also be provided. Additionally, ff land application permitting is being pursued through TRRC, then a soil quality study will need to be conducted over the proposed discharge area.

Additionally, pilot testing of the treatment process should be demonstrated. One goal of the pilot test would be to demonstrate that the treatment technology can reach key performance indicators related to treated water quality, which currently remain to be determined. Pilot testing provides an important opportunity to assess the need for any pre-treatment processes that might be needed to achieve desired treatment performance and robustness of operations.

3.3. FP Utilization and Permitting in Other Pertinent States

While the landscape for discharge permitting of FP in Texas and New Mexico is in its early stages, there is precedence for such operations in other states. A pilot project for Occidental Petroleum involved the use of reversed osmosis and other minor modalities for treatment of low salinity water containing significant total petroleum hydrocarbons (TPH) and ammonia. This process met all NPDES discharge permit requirements, including appropriate WET and ammonia levels. In remote western Colorado, WPX has garnered multiple awards for moving away from transportation of produced water and deep well injection, to the use of RO treatment. There, pilot treatment efforts were shown to meet permitting requirements for effluent water quality. In Wyoming, Encore Green Environmental was authorized for land application of treated produced water, on a 15-acre area in Laramie County, by the Wyoming Department of Environmental Quality. In Oklahoma, Committed Water has been desalinating low salinity flowback and produced water, and discharging it for land application under a permit from the Oklahoma Oil and Gas Conservation Division, for approximately one year. In West Virginia, a 60,000-bpd thermal distillation treatment facility exists, with a landfill being constructed nearby to accommodate the generated solid waste stream from the facility. In California, Chevron has been active for many years. A 25-year agriculture irrigation project has been established with Kern County and the Cawelo Water District to blend treated low salinity produced water with surface water in the district. This particular effort shows significant forward progress in a state that is characterized as having the most stringent regulations and testing/monitoring burden.

4. Municipal Water Treatment: Historical Context

Municipal water is the totality of the public water supply network. This consists of water treatment facilities, water storage facilities (reservoirs, water tanks, and water towers, among others), as well as pipe networks for distribution to residential, industrial, commercial, and institutional establishments. Similar to FP water, municipal water has a wide array of substances, chemicals, and other additives that are found in its composition. These can include disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals, microorganisms, and radionuclides. Some of the major categories of the chemical contaminants are inorganic contaminants (IOCs), volatile organic contaminants (VOCs), and synthetic organic contaminants (SOCs). Common microbial contaminants consist of numerous bacteria, parasite cysts and eggs, viruses, and various strains of fungi [35,36].

Due to its complexity and wide range of uses, municipal water is treated and screened extensively. Some of the basic steps of municipal water treatment described by the EPA and the Centers for Disease Control (CDC) are collection, screening, straining, chemical addition, coagulation, flocculation, sedimentation, clarification, filtration, disinfection, storage, and distribution. However, based on the region and source of the collected water, some of the screening and treatment may not be utilized, as described by the EPA's drinking water requirements for states and public water systems [37]. Recently, wastewater treatment for the removal of physical, chemical, and biological contaminants have used systems and processes such as activated sludge, aerated lagoons, stabilization ponds, natural and synthetic wetlands, trickling filters, and rotating biological contactors (RBCs).

Even though municipal water goes through extensive treatment and screening, the process is not perfect, because it is hard to ascertain the totality of the water content and screen for all possible constituents. Due to this, compromises are made in terms of screening, treatment, and contaminant limits. For example, endocrine disrupting chemicals (EDCs) can be present in municipal water in various forms, such as steroid hormones, pharmaceuticals, personal care products, fluorinated substances, bisphenols, phthalates, pesticides, and natural and synthetic estrogens. In many cases, EDCs are not efficiently removed from municipal water and can actually be created as a by-product of the disinfection stage of water treatment [38,39]. Another issue in municipal water is pipe contamination. In recent years, the distribution system infrastructure has been rapidly deteriorating and has caused increased lead, rust, and microbial contamination in municipal water [40,41]. Additionally, based on the EPA's recent reissue of regulatory determination for perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), these contaminants are to be regulated in drinking water, whereas 1,1-dichloroethane, acetochlor, methyl bromide (bromomethane), metolachlor, nitrobenzene, and RDX will not be regulated.

5. Conclusions

As it currently stands, in a majority of the energy producing states in the US, greater utilization of FP, particularly for beneficial reuse applications, is precluded by a lack of regulatory framework. The absence of permitting processes for beneficial reuse in key states like TX and NM, is reflective of the need for more information on FP treatment. It is necessary to understand 'how clean is clean enough' for treated oilfield effluent to be used as a non-potable source of fresh water. From an analytical perspective, there are numerous parallels between FP and municipal water. Due to their complex biogeochemical compositions, both fluids must undergo similar extensive treatment and screening processes, which ultimately, do not completely remove all of the undesirable constituents. As a consequence, water safety legislation dictates that residual amounts of contaminants are permitted to persist in municipal water, albeit below a set percentage. Additionally, screening processes often do not include measurements for the presence of antibiotics, hormones, and other drugs that may compromise human health. As such, FP has the potential to be managed in a similar fashion, to enable the production of treated non-potable fresh water. However, in order to fully support this paradigm shift, it is our opinion that the development and utilization of surrogate water quality measurements is required in order to assess overall water quality in a time- and cost-effective fashion. Specifically, in situ measurements of TOC and conductivity can be used with predetermined contaminant correlations to facilitate the rapid measurement of hazardous materials that may be present in the water. These measurements, in conjunction with toxicological assays, could serve as powerful tools to determine the suitability of treated FP for various terminal applications. Efforts to this effect could change the landscape of FP management and potentially lay the groundwork for new legislation that supports greater FP utilization in a safe and sustainable fashion.

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