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Review

A Critical Review of Analytical Methods for Comprehensive Characterization of Produced Water

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Abstract: Produced water is the largest waste stream associated with oil and gas production. It has a complex matrix composed of native constituents from geologic formation, chemical additives from fracturing fluids, and ubiquitous bacteria. Characterization of produced water is critical to monitor field operation, control processes, evaluate appropriate management practices and treatment effectiveness, and assess potential risks to public health and environment during the use of treated water. There is a limited understanding of produced water composition due to the inherent complexity and lack of reliable and standardized analytical methods. A comprehensive description of current analytical techniques for produced water characterization, including both standard and research methods, is discussed in this review. Multi-tiered analytical procedures are proposed, including field sampling; sample preservation; pretreatment techniques; basic water quality measurements; organic, inorganic, and radioactive materials analysis; and biological characterization. The challenges, knowledge gaps, and research needs for developing advanced analytical methods for produced water characterization, including target and nontarget analyses of unknown chemicals, are discussed.

Keywords: produced water; water quality; hydraulic fracturing; analytical methods; treatment; reuse

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1. Introduction

In 2020, the United States became a net energy exporter and will remain so until 2050, according to the U.S. Energy Information Administration [1]. Water resource management significantly influences the oil and gas (O&G) industry because water is used for almost all stages in fossil fuel production, such as well drilling and completion, reservoir management, enhanced oil recovery, and hydraulic fracturing (HF) [2]. HF uses a large volume of water to extract O&G from an "unconventional play" (or "tight oil play"), which refers to the low permeable unconventional shale that cannot be explored and produced by conventional processes relying on the natural pressure of the wells and pumping operation [3,4].

At the initial stage of HF, fracturing fluids are injected into deep wells under high pressure to fracture the geological formation, increase permeability, and extract oil and gas. Around 91–94% (mass percentage) of the fracturing fluid is water, with ~5–8% proppant (mostly sand) and ~1% chemical additives [5,6]. After HF, a portion of injected water returns to the surface with high levels of dissolved solids, salts, and chemical additives; this water is often referred to as flowback water (FW). FW usually occurs in the first several weeks and before the well is placed in production. Over time, FW diminishes and is replaced with formation water native to the well, which is referred to as produced water (PW), occurring throughout the life of a well [7]. In the field, FW and PW are commonly co-mingled so that these streams cannot practically be distinguished. Thus, PW is often broadly defined to include both water streams.

The United States produces an estimated 900 billion gallons of produced water (PW) annually, making it the largest waste stream associated with O&G activity [8]. The amount of PW generated per year keeps increasing with unconventional O&G development (UD), which produced more than 50% of crude oil and natural gas in 2019 [1]. The production increase of the UD in the U.S. is mainly from seven key oil and gas basins: Appalachia including Marcellus and Utica (Pennsylvania, Ohio, and West Virginia), Bakken (North Dakota and Montana), Eagle Ford (South Texas), Haynesville (Louisiana and East Texas), Niobrara (Colorado and Wyoming), and the Permian Basin (West Texas and Southeast New Mexico) [9]. The PW from unconventional reservoirs usually cannot be reinjected into the shale reservoir for enhanced recovery but needs appropriate disposal such as into non-oil-producing geologic intervals (e.g., salt water disposal (SWD) wells) [3] or reuse for HF [10]. Approximately 55% of PW generated from conventional and unconventional activities in the U.S. is handled as wastewater for disposal [10]. With the increase in UD, disposal of PW in SWD wells has not only raised concern about surface water and groundwater contamination [11–13] but also risks of increased seismic events [14], such as the UD-related earthquake in the Bend Arch-Fort Worth Basin in northern Texas in 2008 [15]. In addition, the rapid expansion of UD has increased the demand for freshwater resources, which can exaggerate the water shortage in arid regions.

Reuse of PW can reduce freshwater usage and wastewater disposal, thus significantly enhancing the economic benefits and environmental sustainability of O&G production [16–19]. Currently, PW reuse is increasing within the O&G sector to support HF operations, and other potential beneficial uses outside the O&G sector have also been identified [10]. However, PW is considered one of the most complex aqueous mixtures [20]. Detailed characterization of the physicochemical and biological composition of PW is critical to monitor field operation and process, evaluate treatment efficiencies, assess potential risks on public health and environment during PW reuse, and inform management practices and regulatory compliance.

Despite numerous studies on PW analysis, there are no standardized methods approved by the United States Environmental Protection Agency (EPA) [21]. In the Code of Federal Regulations, title 40 (40 CFR), Part 136 (Guidelines Establishing Test Procedures for the Analysis of Pollutants), the EPA identified approved test methods for inorganic analytes (76 parameters), radioactive analytes (5 parameters), non-pesticide organic compounds (120 parameters), pesticides (70 parameters), biological indicators (8 parameters), and aquatic toxicity (4 parameters) [22]. The EPA has published these methods in "Selected Analytical Methods for Environmental Remediation and Recovery (SAM) 2017" [23]. The European Union (EU) has different water quality directives for different water bodies, such as 98/83/EC (drinking water), 80/68/EEC (groundwater), and 75/440/EEC (Surface water). However, these standard water quality analysis methods/directives usually only apply for freshwater (total dissolved solids, TDS < 1000 mg/L) or municipal and industrial wastewater. Since the TDS concentrations in PWs may range from less than 3000 mg/L to over 300,000 mg/L, these highly saline waters are difficult to analyze. Some of the traditional analytical methods do not work accurately for an intricate water matrix like PW. Danforth et al. reviewed 129 articles with detailed chemical analysis for 173 sources of PW collected from 27 locations in North America. They identified 1198 unique chemical constituents in PW, and only 290 (24%) could be quantified by the EPA-approved test methods. They also found that these studies are predominantly focused on the Marcellus Basin in Pennsylvania, even though the majority of produced water volume is generated in areas such as Texas, California, and New Mexico [8]. Thus, the development of suitable analytical methods for accurate PW characterization in complex water matrices is imperative.

This review aims to evaluate the commonly used analytical techniques for qualitative and quantitative analysis of PW. A tiered analytical approach is proposed to meet different operational and regulatory needs. For this critical review, we focused on the papers published after 2012 (and after 2016 for organic analysis) and reviewed 157 peer-reviewed publications and regulatory standard methods. PW compositions compiled from these sources are first presented and compared spatially and temporally to identify the challenges of PW characterization. The analytical techniques used in research papers are then compared with available regulatory standard methods from the EPA, including field sampling and sample preservation methods and pretreatment methods, basic water quality measurements, inorganic and organic analysis, radioactive measurements, and biological analysis. Based on the assessment of analytical tools, suitable analytical procedures are proposed to characterize PW samples. The review also identifies knowledge gaps and research needed to improve future PW characterization methods.

2. Water Composition

The physical and chemical properties of PW generally vary noticeably based on the geographic location, geologic formation, source oil, and chemical additives selected by a drilling company (spatial variation). These properties also depend on the time the PW samples are collected after well completion (temporal variation). The water constituents of the initial FW differ significantly from the PW [24]. Oetjen et al. examined the water chemistry of an HF site in the Niobrara formation (Colorado) throughout the flowback period and used principal component analysis to identify different stages in the flowback period [25]. For the well investigated, the majority of FW usually occurred in 1–2 days, the transition stage could last 6–21 days, and the PW stage generally started after 21 days [25].

Because PW contains a large portion of formation water, it generally contains native or geogenic constituents associated with the geological formation. In addition, many different chemical additives are injected into the wells during HF. Thus, the chemical constituents of PW often come from two sources: native constituents from the geologic formation and chemicals from fracturing fluids [5]. Native constituents often include salts, oil and grease, naturally occurring radioactive materials (e.g., radium, radon, strontium, uranium, and thorium), inorganic substances (e.g., ammonia and hydrogen sulfide), metals (e.g., aluminum, arsenic, barium, sodium, potassium, iron, and zinc), volatile gases (e.g., CH_4 and CO_2), and hydrocarbons (e.g., alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs) and phenols) [5]. Another essential constituent in PW is bacteria, which are ubiquitous in the environment. They can originate from the geological formation itself, the source water used to create the fracturing fluid, and the associated infrastructure. [26].

Table S1 in Supporting Information (SI) summarizes the general physicochemical parameters of PW quality from primary UD plays in the U.S. PW from Bakken, Barnett, and the Permian contains high TDS (average >140 g/L) and relatively low dissolved organic carbon (DOC, average ~100 mg/L). In contrast, the water from Niobrara shows opposite trends, lower TDS (~40 g/L) and higher DOC (~1000 mg/L). The composition of PW also changes significantly during the well production process. Figure S1 in Support Information shows the temporal change of PW quality in Marcellus formation in Pennsylvania and Niobrara formation in Colorado. Because of the higher proportion of formation brine, PW typically has considerably higher TDS concentrations than FW. However, FW can have higher organics due to organic additives in fracturing fluid [24,27,28].

The primary types of organic additives used in HF fluid have been reported [6,7,10] and are publicly available on the FracFocus website. Table 1 summarizes the commonly used chemical additives, including acid, biocide, breaker, clay stabilizer, corrosion inhibitor, crosslinker, friction reducer, gelling agent, iron control, non-emulsifier, pH adjustment agent, scale inhibitor, and surfactant. It is important to note that the total chemical additives in HF fluid are only up to 0.5–1%. However, these unique chemicals can be used to track the PW related to UD. Although significant efforts have been made to disclose chemical additives used during HF, some additives are only identified by their generic names or are protected by proprietary claims such that sufficient information to identify the chemical structure is not made publicly available. To date, the identities of a fraction of the chemicals used in fracturing operations remain unknown. Identifying and detecting these additives present a particular challenge for environmental monitoring.

Table 1. Common groups of chemical additives in HF fluid.

Additive	Example of Chemical	Chemical Purpose	Concentration (of Total Fluid)
Acid	Hydrochloric acid	Help dissolve minerals and initiate cracks in the rock	0.07–0.15%
Biocide	Glutaraldehyde	Eliminate bacteria that produce corrosive by-products	0.075–0.06%
Breaker	Ammonium persulfate	Allow a delayed break down of the gel	0.02–0.06%
Clay stabilizer	Choline chloride	Prevent clays from swelling or shifting	0.05–0.2%
Corrosion inhibitor	Methanol	Product stabilizer and/or winterizing agent	0.002–0.004%
Cross-linker	Petroleum distillate	Carrier fluid for borate or zirconate crosslinker	0.007–0.032%
Friction reducer	Polyacrylamide	"Slick", the water to minimize friction	0.05–0.07%
Gelling agent	Guar gum	Thicken water to suspend the sand	0.05–0.5%
Iron control	Citric acid	Prevent precipitation of metal oxides	0.006 −0.011%
Non-emulsifier	Lauryl sulfate	Prevent the formation of emulsions in the fracture fluid	
pH adjusting agent	Sodium hydroxide	Adjust the pH of the fluid to maintain the effectiveness of other components, such as crosslinkers	0.01–0.011%
Scale inhibitor	Sodium polycarboxylate	Prevent scale deposits in the pipe	0.075–0.12%
Surfactant	Lauryl sulfate	Increase the viscosity of the fracture fluid	0.05–0.1%

Note: Data sources: references [5,6] and information from FracFocus, 2020 (https://fracfocus.org/chemical-use/what-chemicals-are-used).

The bacteria in PW also vary with the location, overall well condition, and well age [29]. Numerous studies investigated the microbial community composition and functional potential across the PW because of bacteria, such as sulfate-reducing bacteria, iron-oxidizing bacteria, and acid-producing bacteria. These bacteria in PW can cause corrosion, fouling, and sulfide release, resulting in production interruptions, harmful environmental consequences, and potential risks to public health [30,31]. Generally, the bacterial communities in the pre-fracturing (groundwater or surface water) fluid are mostly from the classes of *Alpha-proteobacteria* and *Gamma-proteobacteria*. During HF, the aerobic surface water microbial community rapidly transits to the halophilic, fermentative, and anaerobic microbial community in PW because of the extreme conditions, such as high salinity. Salinity is a major factor controlling the bacterial community composition in an aquatic environment [32]. Despite the use of biocides in HF fluid, high bacterial cell counts have been identified in PW. In the Marcellus and Bakken Shale, the microbial abundance in PW varied between 10^1 and 10^4 16 S rRNA gene copies/mL while it was 10^6 to 10^7 copies of the 16 S rRNA gene/mL in the pre-fracturing fluids [26,33,34]. The reasons may be related to the low efficiency/dosage of biocides, and the recycling of PW for HF may cause the enrichment and growth of bacteria [26]. The dominant bacterial classes found in PW include *Alpha-proteobacteria*, *Beta-proteobacteria*, *Epsilon-proteobacteria*, *Gamma-proteobacteria*, *Clostridia*, *Bacilli*, *Synergistetes*, *Bacteroides*, and *Flavobacteria* [26,35]. The dominant bacterial order found in Marcellus Shale was *Halanaerobiales*, followed by *Clostridiales*, *Campylobacterales*, *Rhodobacterales,* and *Bacillales* [36]. Hull et al. investigated the bacterial community succession in the Denver-Julesburg (DJ) Basin (Niobrara shale formation, Colorado). They found that class *Gamma-proteobacteria* was dominant in groundwater (62%). However, the PW sample collected four days after flowback began was dominated by *Thermoanaerobacter* of *Clostridia* (97%), and its relative abundance decreased as *Thermovigra of Synergistia* and *Thermotoga* of *Thermotogae* started to increase at day 55 and 80, respectively. After 220 days, the dominant classes in PW were *Clostridia* (50%) and *Thermotogae* (40%) [37].

As shown by the data and discussion above, PW appears to exhibit a considerable variation in general physicochemical and biological properties. Better characterization of the constituents in PW by location and time is critical to monitor process operation, choose proper management and treatment methods, and guide beneficial PW uses.

3. Tiered Analytical Approach

Figure 1 illustrates the life cycle of produced water management from HF, production, gathering and transportation, treatment, storage (e.g., above-ground storage tank (AST) and recycle impoundments), sourcing and blending, chemical additions, reuse for

HF, advanced treatment (e.g., desalination) for beneficial applications, to waste disposal (e.g., solids to landfill, concentrate to underground injection control (UIC) disposal wells). Analytical testing is necessary throughout all stages and levels of the water cycle. The analytical data will be used to characterize influent streams, model potential technology applicability, monitor process performance, and assess environmental and public health risks of treated water applications and treatment waste streams. There is a need for both rapid testing techniques to support process quality assurance (QA) as well as more detailed characterization testing for proper disposal, treatment, and reuse. As a result, we propose a multi-tiered approach and classify the PW analysis into four main tiers (Table 2) based on the needs to meet different purposes of analysis, cost, complexity, and turn-around time (Figure 2).

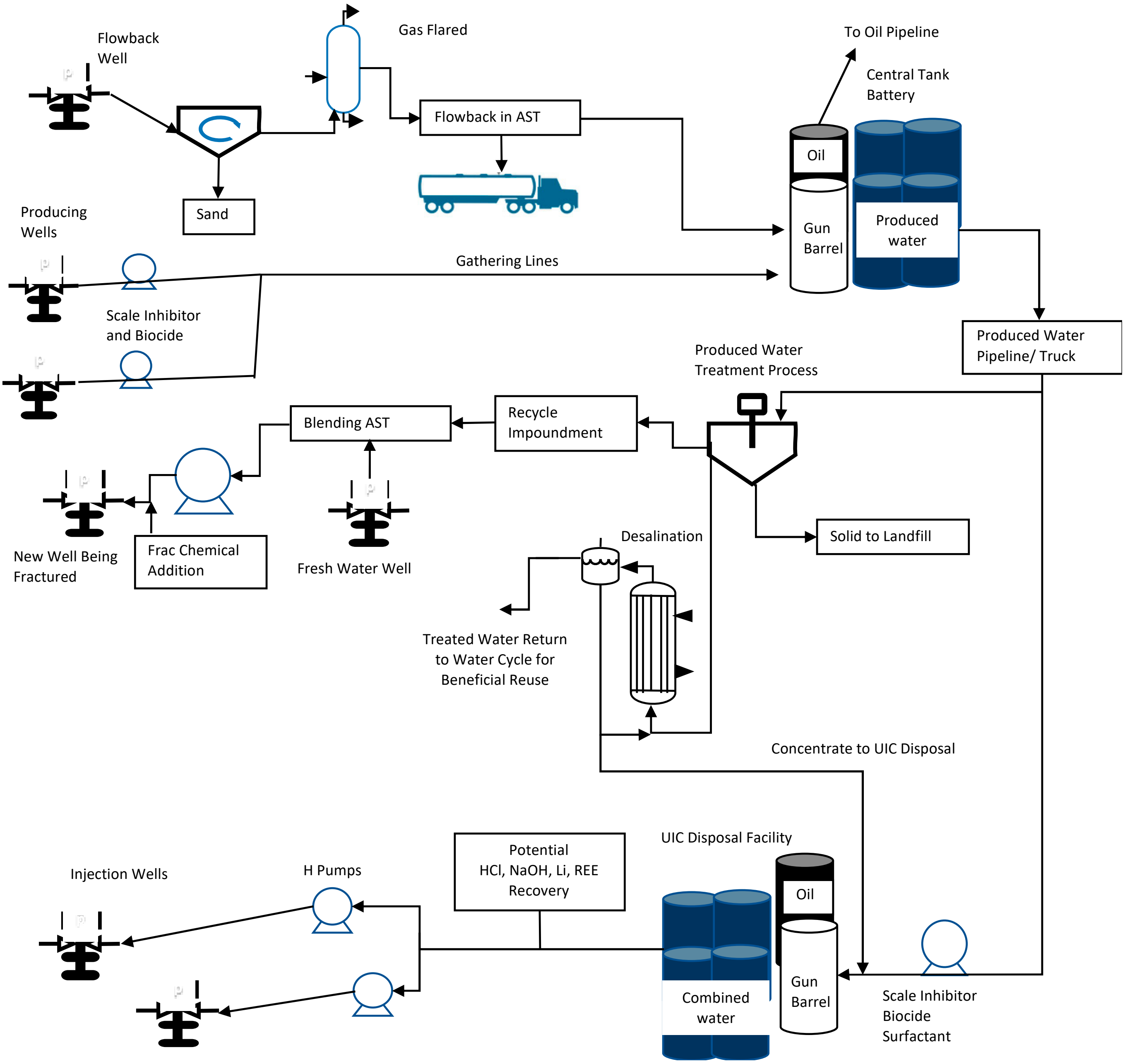

Figure 1. Schematic diagram of produced water production, transportation, treatment, reuse for hydraulic fracturing, advanced treatment for beneficial uses, and disposal. AST: Above surface storage tank; UIC: underground injection control.

Table 2. Multi-tiered approach for produced water characterization.

Level	Use	Description	Parameters	Frequency
Tier 1	Continuous monitoring, bulk testing, KPI rapid analysis, process control	In-Line Sensors Field Parameters Filter Analysis	Flow, TSS, TDS, TOC, pH, ORP, iron, H_2S, TPH, level sensing, carbonate	Realtime, continuous, and routine
Tier 2	Detailed characterization, routine monitoring, and Tier 1 data verification	Conventional Lab Testing	Wet chemistry, ICP-OES, ICP-MS, GC, GC-MS, HPLC	Baseline, quarterly, when experiencing data excursions in Tier1. Proving up treatment efficacy and reliability, beneficial reuse investigation
Tier 3	NPDES discharge compliance, modeling treatment technology; Waste disposal profile generation; Risk assessment and data capture for fate/transport modeling.	Unconventional Lab Testing; WET Testing Leachate Testing Bio-mobility and accumulation testing	LC-MS, Gamma Spec, High Res GC-MS; Acute and chronic toxicity TCLP, SPLP, LEAF testing of residual waste Tier 1,2,4 analysis of treated effluent on soil, plant, tissue samples	When evaluating technology and management processes. As per permit/regulatory agency
Tier 4	Source apportionment, fingerprinting	SEM/EDX, XRD, FEEM, biomarker analysis, isotopic analysis		Evaluating technology and management process. Basic research for method development. Event response. Beneficial reuse investigations.

Note: TSS: total suspended solids; TDS: total dissolved solids; TOC: total organic carbon; ORP: oxidation reduction potential; TPH: total petroleum hydrocarbon; ICP-OES: inductively coupled plasma-optical emission spectroscopy; ICP-MS: inductively coupled plasma-mass spectroscopy; GC-MS: gas chromatography-mass spectroscopy; HPLC: high-performance liquid chromatography; LC-MS: liquid chromatography–mass spectroscopy; TCLP: toxicity characteristic leaching procedure; SPLP: synthetic precipitation leaching procedure; LEAF: Leaching Environmental Assessment Framework; SEM/EDX: scanning electron microscopy/energy dispersive X-ray spectroscopy; XRD: X-ray diffraction; FEEM: Fluorescence excitation-emission matrix.

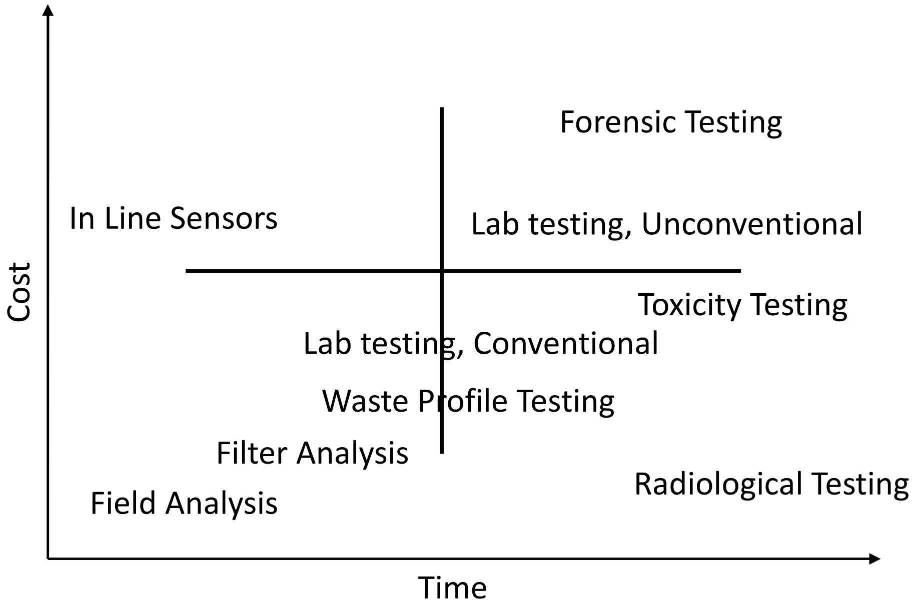

Figure 2. The cost and turnaround time of produced water analysis.

Tier 1 analysis involves using in-line sensors, field parameters, and onsite testing for real-time, continuous monitoring, and routine process control. An efficient indicator system could be established with key performance indicators (KPIs) to support the control of operations and processes within certain limits and for internal and external reporting. The KPIs need to be formulated from different perspectives depending on the operation and process. They may include flow, total suspended solids (TSS), conductivity/TDS, pH, temperature, oxidation-reduction potential (ORP), iron, H_2S, alkalinity, total organic carbon (TOC), suspended and colloidal particles, and total petroleum hydrocarbon (TPH). One challenge for Tier 1 analysis is to maintain the accuracy of these in-line sensors, which are installed under harsh conditions. Routine calibration/replacement is required to ensure high-quality data. Another challenge is the data analysis/classification from these in-line sensors. Advanced statistical methods, software tools, machine learning, and connected digital systems are required for data processing, failure analysis, predicting performance, and operation control. An excursion from historical control limits detected by in-line Tier 1 sensors will trigger grab sample capture and Tiers 2 to 4 characterization analysis. Tiers 2 to 4 focus on detailed characterization, routine monitoring and Tier 1 data verification, National Pollutant Discharge Elimination System (NPDES) permit compliance, evaluating treatment technology and management processes, and as per permit/regulatory agency for beneficial uses, or event responses. Conventional and unconventional lab testing, Whole Effluent Toxicity (WET) testing, leachate testing, and fingerprint testing will be conducted using advanced analytical tools. For example, ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry (ICP-OES) analysis can provide elemental and ionic makeup of TDS. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) can provide information about particle size, morphology, and crystal structure. A variety of techniques can be employed to characterize the same common parameters at different levels.

4. Field Sampling, Preservation, and Sample Pretreatment

4.1. Field Sampling and Preservation

Environment sampling is a crucial process to ensure the certainty of analytical results. Several important aspects need to be considered for the field sampling process, including sampling points and locations, analyte selection and the number of samples, field measurements and sampling log, containers and preservation, quality assessment samples, and other related information.

Sampling points and locations should represent the PW management process and have to be consistent to ensure that the results from a different period of measurements are comparable. Common sampling points include wellhead, oil-water separator, storage tank, and points before and after treatment, as shown in Figure 3. Several parameters should be measured during the sampling process when each sample is collected to estimate the sample variation and guide sample preservation methods, such as temperature, pH, free chlorine residual, gross density, and conductivity. Free chlorine measurements will be used to guide the sample preservation.

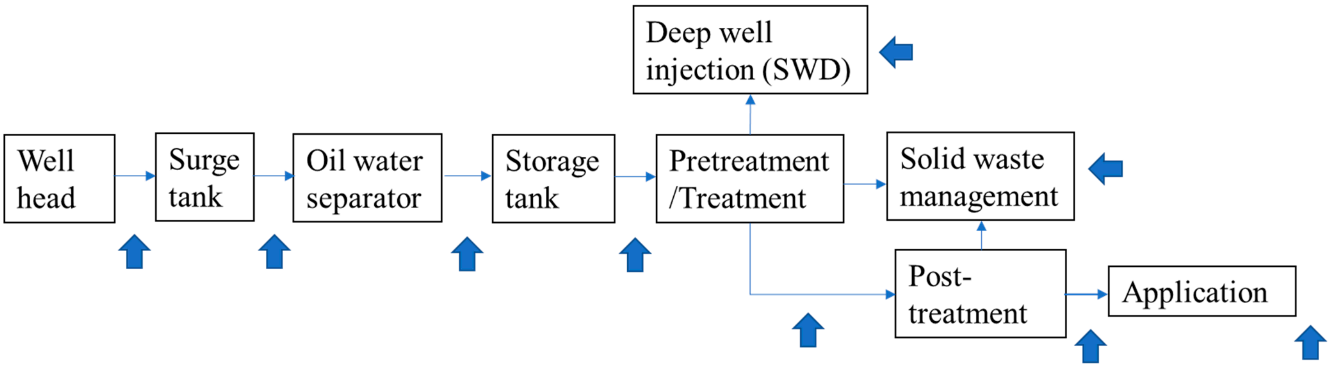

Figure 3. Example of water sampling and analysis locations and tiers.

The details of different sample containers and preservation methods for the target analytes are discussed in Support Information. Based on the methods generally used by commercial labs under the EPA guidance, Table S2 summarizes the analytical methods, containers, preservations, and holding times for PW analysis of wet chemistry, anions, total metals, organics, radioactive, and WET testing.

4.2. Sample Preparation and Pretreatment

Sample preparation is essential for PW analysis. It has several goals: (1) to concentrate or dilute target analytes to meet the capability of analytical instrumentation; (2) to remove materials in the matrix that might interfere with the chromatographic separation, ionization, or detection of target analytes. For inorganic analysis, these goals are usually met by removing particles and diluting the sample to meet instrument performance. For organic compound analyses, removing inorganic ions in PW while retaining specific organics in the final solution is often required. The EPA's SW-846 compendium consists of over 200 analytical methods for sampling and analyzing waste and other matrices. It includes the 3000 series for inorganic sample preparation, 3500 series for organic sample extraction, and 3600 series for organic extract cleanup. A variety of sample preparation methods suitable for PW samples are discussed in the following sections.

4.2.1. Liquid-Liquid Extraction and Solid-Liquid Extraction

Liquid-liquid extraction (LLE) is currently the most widely used organic compounds extraction method for PW, especially to extract semi-volatile compounds for gas chromatography (GC) analysis, due to its simplicity and ease of method development [38,39]. It has also been widely used in EPA-approved methods to extract GC amenable organic compounds in water samples (solid-liquid extraction is used for solid samples, discussed below), such as in EPA Method 625. It usually uses an organic solvent to extract non-polar compounds from PW, targeted non-polar analyte can be collected from the organic solvent, and the hydrophilic analyte is left in the PW matrix. The most widely used organic solvent for LLE in PW analysis is dichloromethane (DCM), the recommended solvent in the EPA methods. LLE has several limitations when applied to treat PW samples. First, it has low selectivity; the analyte is often extracted with other compounds, which increases background noise. When a large number of interferences exist in the extract, a cleanup step is required.

The cleanup procedure of the silica gel column is recommended in the EPA Method 610. Second, when LLE is used to collect water-soluble compounds, dilution is often required to deal with the high TDS in the water matrix, which increases the minimum detection limit (MDL) for the analyte. Finally, the most considerable disadvantage of this method is the formation of emulsions during extraction, especially for PW samples, which contain large amounts of surfactant-like compounds. The surfactant creates a mid-phase, making the clean collection of one phase difficult [40,41]. However, emulsions can be reduced by using a continuous extractor as described in the EPA Method 625 or adding salt into the solution, as salt changes the capacity of the aqueous phase, driving slightly soluble compounds into the organic phase. Salt-assisted LLE is more widely used to extract organics from PW samples [25,42].

Solid–liquid extraction (SLE) can extract analytes from contaminated soil or other solids related to O&G activities. Organic solvent and solid are usually mixed under ultrasonic, which increases extraction yield and decreases extraction time (EPA Method 3550C). The mixture is then centrifuged, and the supernatant is collected for further treatment. Accelerated solvent extraction (ASE) is an SLE method for extracting various chemicals from a complex solid or semisolid sample matrix. It uses high temperature and pressure to accelerate the extraction process further, increase extraction yield, and decrease the amount of solvent required [43]. SLE and ASE have been used to extract organics adsorbed on particulates in PW for a comprehensive analysis of the total organics in PW samples [13]. Soxhlet extraction (EPA Method 3540C) is also a widely used method for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. It uses a Soxhlet extractor to ensure intimate contact of the sample matrix with the extraction solvent, which improves extraction efficiency to extract targeted compounds from solid matrices.

4.2.2. Solid-Phase Extraction

Solid-phase extraction (SPE) is a powerful and widely used extraction technique that offers high selectivity, flexibility, and automation. The EPA Method 3535A is a procedure for isolating target organic analytes from aqueous samples using SPE media. SPE has been widely applied to concentrate and purify analytes from different water matrices, including wastewater and PW [25,31,44]. It can easily remove the interferences (such as salt, insoluble material, and unwanted organics) in PW without the formation of emulsion and allow concentrating the analyte during sample preparation to decrease the MDL, which is crucial to meet environmental regulations. It can also be used to collect different groups of compounds from one SPE column based on their polarity. Sorensen et al. collected nonpolar compounds from the SPE column first by using n-hexane followed by DCM, and then the polar part was collected by using methanol (5–20%) in DCM as an elution solvent [45]. Some researchers also used SPE to remove hydrophobic compounds in samples for IC analysis [46]. One disadvantage of this technique is that it requires more knowledge about the targeted analytes than other approaches. It requires more effort to find suitable sorbents and solvents when dealing with an unknown sample. Furthermore, the cost of the SPE is higher than that of other techniques [40]. Table S3 in Support Information summarizes the SPE cartridges used in literature for organic analysis.

Solid-phase microextraction (SPME) is an SPE technique that uses a fiber coated with an adsorbent material to extract analytes from the liquid or gas phase. After extraction, the SPME fiber is transferred to the injection port of separating instruments, such as GC, LC, or mass spectroscopy (MS), where desorption of the analyte takes place. SPME has several advantages, such as (1) it does not require a solvent and purge-and-trap instrument (discussed in the following section), which saves time and money; (2) it can be highly selective based on the fiber and adsorbent used for the analytes [38,40]. Khan et al. used SPME to pretreat PW samples from the Permian Basin and successfully characterized 1400 compounds, including benzene, toluene, ethylbenzene, xylenes (BTEX), alkanes, and alkylbenzenes [20]. Almaraz et al. used a polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber to extract five different iodinated organic compounds (chloroiodomethane, diiodomethane, triiodomethane, chlorodiiodomethane, and bromodiiodomethane) from PW. The extracted compounds were then analyzed by headspace gas chromatography-mass spectrometry (GC-MS). The fiber material, extraction temperature and time, and desorption time were also evaluated [47]. Redman et al. also used SPME for quantitative analysis of nonpolar and organic acids in PW, which can then be linked to toxicity prediction [48].

Fabric phase sorptive extraction (FPSE) is a new type of SPE, similar to SPME [49]. It uses small squares of cellulosic (or other) fabric coated with an ultrathin sol-gel to sorb and extract analytes directly from aqueous environmental water samples. The analyte is then eluted from the fabric piece by a small volume of extraction solvent and injected into a chromatography system [50]. FPSE offers several advantages of short extraction times, minimal solvent use, and the ability to reuse coated fabric pieces after minimal cleaning. FPSE has been successfully applied to drinking water, surface water, wastewater, and biological samples; however, there is no publication using it for PW analysis [51].

4.2.3. Other Methods

Purge and trap is suitable for GC analysis. It is widely used in EPA-approved methods to extract organics from water and wastewater, such as the EPA Method 624.1. The sample is first placed in a sealed vessel; inert gas is purged into the sample to cause volatile compounds to be swept out. The gas with volatile compounds is passed through an adsorbent trap, where the volatiles are retained. The final step is to desorb the volatiles by heating the trap and using GC carrier gas to inject them into a GC instrument.

Derivatization is a useful sample preparation tool for organic analysis. It converts a specific compound into a product of a similar structure that is more suitable for analysis. A chromophore can be added to a compound to enable its detection in UV-Vis spectrophotometry. A polar or nonpolar group can be used to adjust the retention time of a compound in GC or LC, thus enhancing the separation efficiency. Derivatization can also be used to improve ionization efficiency for poorly ionizable compounds in MS [52]. Derivatization with 2, 4- dinitrophenylhydrazine is the recommended approach to analyze aldehydes, such as glutaraldehyde and formaldehyde; both are used as biocides in HF fluids [53,54]. Sorensen et al. used N,O-bis(trimethylsilyl)trifluoroacetamide (BSFTA) to derivatize all the acidified organic compounds extracted from PW for nontarget analysis, and BSFTA is used to protect the labile groups such as hydroxyl in the target analytes [45].

In summary, proper sampling and preservation are vital to analyzing the chemical constituents accurately in PW. Due to the complex PW matrix, sometimes multiple sample pretreatments are required to collect the target analytes. For example, LLE can be used as a first step to extract all the organics from liquid samples, and then the extract is further cleaned by SPE [13]. Alternatively, PW samples can be first acidified (HCl, pH < 2) to prevent degradation, followed by LLE (DCM) to extract all the organics from the water samples. The extract can then be further cleaned and separated by SPE for characterization by different analytical methods [45].

5. Bulk Measurements and Basic Water Quality Parameters

Bulk measurements are essential for any water analysis because they are quick and cost-effective and provide overall information about the water matrix. The informative bulk measurements include pH, conductivity, temperature, alkalinity, salinity, total suspended and dissolved solids (TSS and TDS), total organic carbon (TOC)/dissolved organic carbon (DOC), total nitrogen (TN), total petroleum hydrocarbons (TPH), oxidation-reduction potential (ORP), and others [55]. These basic parameters are valuable for monitoring well operation and guiding subsequent detailed analysis. Some industries use these parameters as process control, only performing a more detailed analysis when fluctuation is observed [56]. These measurements can be performed on-site with probes/sensors or in the lab with a relatively simple instrument. Currently, there are commercial probes available for on-site measurements. For example, YSI Professional Plus multi-parametric probe can be used to measure temperature, dissolved oxygen, conductivity, TDS, salinity, pH, turbidity, and ORP [30]. Please refer to SI for detailed discussions on basic PW quality analysis. Table S1 includes some measurement results of the typical water quality parameters from different PW sources.

6. Organic Analysis

As discussed in Section 2, dissolved organic matter (DOM) in PW usually derives from a combination of native hydrocarbons (e.g., BTEX, PAHs, phenols, humic and fulvic acids), chemical additives (e.g., biocides and guar gum), and the transformation products under extreme conditions in the well (high temperature and pressure). Synthetic organic compounds from source water for well operation have also sometimes been detected. Alcohols (made up mostly of methanol) are the most abundant organic compound group in PW (approximately 91% of total volatile organic concentration) [57]. The organic constituents vary widely during the lifetime of the well operation, especially during the early stage of well drilling. Sun et al. investigated the organic content in PW in the Duvernay formation (Alberta, Canada). They found that most organic compounds declined in abundance over the first nine days of flowback, except certain kinds of compounds such as phthalate diesters and hydroxyquinoline, which were still observed on Day 30 [58].

Bulk measurements such as DOC, COD, and ultraviolet absorbance at 254 nm ($UV_{254\ nm}$) are convenient techniques to estimate the total DOM in aqueous samples. There are also several advanced analytical techniques for characterizing and quantifying DOM, including gas chromatography coupled with flame ionization detector (GC-FID), thermal conductivity detector (GC-TCD) or mass spectrometry (GC-MS), and liquid chromatography (LC) coupled with UV-diode array detector (LC-UV), organic carbon detection (LC-OCD) or mass spectrometry (LC-MS). GC-based methods are extensively used to analyze volatile and semivolatile organic compounds (VOCs and SVOCs), including natural gas constituents (methane and ethane), BTEX, diesel range semivolatile organics with detailed discussion in Section 6.2. LC-based techniques are more suitable for non-volatile organic compounds such as surfactants, fatty amines, high molecular weight ionic polyacrylamide friction reducers with detailed discussion in Section 6.3 [21].

One of the significant challenges to analyze organic compounds in PW is the lack of standardized and validated methods. There are EPA-approved standard methods for domestic and industrial wastewater, and they may be suitable for some PW analyses. For example, the EPA Method 610/Method 8275A/8270 SIM for determination of PAHs, which exist in PW, by both HPLC-UV and GC-FID; the EPA Method 553 for determination of Benzidines and Nitrogen-containing pesticides (used as chemical additives in HF fluids) in water by LLE or LSE and HPLC-MS are all plausible methods. However, they have not been validated to handle the PW matrix, which can be four times saltier than seawater. The EPA approved methods target specific or a series of known organic compounds, while numerous unknown organic compounds may exist in PW, which requires the development of new methods or modification of existing methods. The identification and quantification of individual organic compounds among the complex matrix of PW require various sample preparations (Section 4) and advanced analytical techniques [59].

6.1. Mass Spectrometry, Tandem Mass Spectrometry, and High-Resolution Mass Spectrometry

Mass spectrometry (MS) is the most potent detector to characterize complex fluids and has been extensively used for PW analysis. It can provide qualitative and quantitative information about the analytes with the help of standards or mass spectral libraries. MS identifies charged analytes that are produced by ionization through a mass analyzer. Different ionization methods and mass analyzers provide different benefits and analytical power.

There are several ionization methods, including electron ionization (EI), chemical ionization (CI), electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and matrix-assisted laser desorption/ionization (MALDI). EI is the most common ionization method for GC analysis. Numerous studies used EI to investigate the VOCs and SVOCs in PW [60]. Because EI is a hard ionization method that breaks almost all the parent ions into fragments and leaves a small amount or no parent ion, it is difficult to identify the parent ion without standards or a library of MS fragmentation spectra [61]. On the other hand, the EI spectra are very reproducible when the "standard" EI settings are used, regardless of the equipment. Thus, substantial effort has been devoted to developing GC-MS libraries with EI using standardized conditions. Today, GC-(EI)-MS libraries contain hundreds of thousands of compounds for researchers to identify unknown compounds, such as the Wiley database with ~600,000 compounds and the NIST/EPA/NIH mass spectral library for EI-spectra containing ~267,376 compounds [62].

CI is a soft ionization method that does not break the parent ions into fragments; thus, more parent ions will remain. This property may help identify unknown compounds. However, to date, it has not been used in PW analysis. ESI and APCI are both soft ionization methods to couple LC and MS. ESI is the most commonly used ionization method for LC-MS, and there is no literature reported using APCI for PW analysis. While EI generates radical cations, ESI usually generates protonated/deprotonated or adduct ions (Na^+-, K^+-), which depends on the characteristics of the analyte and the experimental conditions. There are three major issues with ESI for PW analysis. First, some compounds (such as surfactant) will interfere with the ionization of other compounds. Second, a high concentration of sodium (and other ions) in PW usually generates unpredictable adducts during ionization, hindering quantification. Third, LC-(ESI)-MS libraries are at a much smaller scale compared to GC-(EI)-MS libraries, due to lack of standardization for MS conditions and differences in spectra generated on different brands and types of mass spectrometers and also because it was developed more recently [41,62]. MALDI is a soft ionization method that uses a laser energy absorbing matrix to create ions from large molecules with minimal fragmentation. It has been widely applied to the analysis of biomolecules and large organic molecules and has also been applied to identify microorganisms in PW, as discussed in Section 7 [30,63].

Standard mass analyzers include the magnetic sector, quadrupole (Q), ion trap, and time of flight (ToF) mass analyzer. The general characters of each mass analyzer are summarized in Table 3. The quadrupole is the most commonly used mass analyzer for PW samples because of its availability to researchers and good performance [41]. It consists of four precisely matched parallel metal rods, and a high-frequency oscillating electric field is created in these rods. By adjusting the electric field, only selected ions can pass through the geometry of quadruple rods. This approach has many advantages, including high reproducibility, easy to couple with GC or LC, and relatively low maintenance. A significant disadvantage of this detector is its low resolution, which means it cannot separate compounds with close molecular mass and leads to false-positive identifications in mass spectral libraries. The situation worsens when a large variety of compounds exist in a PW sample. ToF is the second most broadly used mass analyzer for PW samples; its performance is better than Quadrupole (Table 3). It separates the ions by the times they needed to travel through a long field-free flight tube; larger mass ions move slower and need more time to reach the detector. It is usually coupled with LC to identify surfactants in PW. It has been crucial in identifying polypropylene glycols, polyethylene glycols (PEGs), and ethoxylated surfactants [64,65]. Ion trap mass analyzers use oscillating electric fields or radiofrequency to trap and separate ions. They can achieve very high resolution but are limited in their capacity to trap ions. The standard configurations include the Quadrupole ion trap, Orbitrap, and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Orbitrap and FT-ICR have very high resolution and become more critical and popular for PW analysis.

Table 3. Comparison of standard mass analyzers [66,67].

	Magnetic Sector	**Quadrupole**	**Quadrupole Ion Trap**	**Time of Flight (ToF)**	**Orbitrap**	**FT-ICR**
Mass range (Da)	15000	4000	4000	Unlimited	$>10^4$	$>10^4$
Resolving power	10^2–10^5	4000	10^3–10^4	15,000	$>10^5$	$>10^6$
Mass accuracy (ppm)	1–5	100	50–100	5–50	2–5	1–5
Scan speed (Hz)	0.1–20	1–20	1–30	10^1–10^6	10^{-1}–10^1	10^{-2}–10^1
MS/MS	Excellent	Great	Great	Great	Great	Great
Cost	$$$$	$	$	$$–$$$	$$$	$$$$

Tandem mass spectrometry (MS/MS) requires two or more mass analyzers coupled in series that are separated by a collision cell to provide fragmentation of selected ions (parent ions) [66]. Conventionally, this technique is best applied for quantitative analysis of specific ions or compounds. It can also provide structural information and further confirm the identity of the unknowns. Common MS/MS include ion-trap, triple-quadrupole (QQQ), and quadrupole-time-of-flight (Q-ToF). When a low-resolution mass analyzer is used, it only acquires nominal masses and can hardly be used for nontarget analysis. However, when paired with high-resolution mass spectrometry (HRMS), MS/MS can provide crucial information to elucidate the elemental composition and structure of the compounds in the sample matrix [41].

HRMS has been successfully applied for discovering unknown contaminants in environmental (and other) samples and will continue to play a key role in identifying new unknown compounds in PW because of its remarkable ability to provide rich structure information that enables compound-specific determinations [68,69]. Currently, the most widely used HRMS/MS includes Q-ToF, Orbitrap mass analyzer, and FT-ICR-MS. However, confidence in the HRMS-based identifications varies between studies and compounds because it is not always possible to find the standards or confirm them via complementary methods. Thus, Schymanski et al. proposed identification confidence levels in HRMS, which have been widely accepted by researchers. The confidence levels are classified into (1) Level 1 (highest confidence), confirmed structure, where the proposed structure can be confirmed by appropriate measurement of a reference standard with MS, MS/MS, and retention time matching; (2) Level 2, probable structure, Level 2a involves unambiguous spectrum-structure matching with literature or library spectrum data, while Level 2b applies when no standard or literature information is available for confirmation, but no other structure fits the experiment information; (3) Level 3, tentative candidate, where evidence exists for possible structure(s), but the exact structure cannot be confirmed; (4) Level 4, unequivocal molecular formula, where a formula can be unambiguously assigned based on the spectral information, but no possible structure(s) can be proposed; (5) Level 5 (lowest confidence), exact mass (m/z), where exact mass can be measured but lack information to assign even a formula [70].

Confidence Level 2 (library matching) is a more convenient method to identify unknown compounds than Level 1 due to the problem of the standards that are not always available, and sometimes the standards can be costly [13,58]. As a result, many separate open and semi-open mass spectrometry databases exist, such as Metlin, MassBank, European MassBank, MassBank of North America, the Global Natural Products Social Molecular Networking (GNPS), and ChemSpider. Two commercial MS/MS libraries, NIST and Wiley, are also available. The NIST20 library database released in June 2020 contains MS/MS spectra for 31,000 compounds, 186,000 precursor Ions, and 1.3 million spectra [71], while the Wiley's MSforID database contains MS/MS spectra for >1200 compounds [51].

Some disadvantages limit the application of MS in PW analysis. The most important reasons are the high capital and maintenance costs, the requirement for well-trained researchers, the lengthy sample analysis and data processing time, and the expensive MS database and standards discussed above. Besides, this technique has some intrinsic drawbacks for PW analysis. First, the resolution of standard mass analyzers decreases with the increases of ions, which means it is essential to separate target analytes from background ions and matrix in PW prior to injection. Thus, significant sample pretreatment (cleanup) is always required in order to achieve acceptable results. Second, the ionization efficiency varies between different compounds and is strongly affected by the sample matrix, especially for ESI. Inorganic or organic matrix constituents that co-eluted with target analytes from LC may enhance or suppress the ionization of the target analytes. The complex matrix chemistry can affect how a target analyte is ionized. For example, an analyte may form a disproportionate amount of sodium adducts $[M + Na]^+$ during ESI when present in saline PW samples instead of forming protonated adducts $[M + H]^+$ when present in clean water matrix, especially for some additives because of their oxygen-rich structures [54]. Sodium adducts pose a problem for typical quantification methods because they do not fragment and protonate adducts [65,72]. This problem limits the application of existing LC-ESI-MS methods for quantifying organics in untreated PW samples, especially the PW sample matrices change over location and time; thus, standard methods are even harder to establish.

6.2. Volatile and Semi-Volatile Organic Analysis

Volatile organic compounds (VOCs) are organic chemicals with a high vapor pressure at ordinary room temperature (low boiling point), while non-volatile organic compounds, in contrast, have a low vapor pressure. Semi-volatile compounds (SVOCs) are the compounds with a vapor pressure between VOCs and non-volatile compounds [73]. In general, more effort has been focused on the analysis of VOCs and SVOCs in PW, which are more amenable to GC for the analysis of non-volatile compounds. Headspace gas chromatography (HSGC) is a convenient method to analyze VOCs such as methanol and ethanol in PW because it reduces the required sample preparation and minimizes matrix interferences. HSGC injects headspace gas, from the top of a sealed container containing a liquid or solid brought to equilibrium, directly into a GC column for separation and analysis. HSGC can also analyze VOCs in contaminated soil near shale basins for UD [74]. The VOCs and SVOCs can be analyzed by GC coupled with numerous types of detectors. One of the most commonly used non-selective detectors is the flame ionization detector (FID), which detects the organic compounds eluted from a separation column. GC-FID is used in the EPA Method 8015 to detect alcohols and organic acids [75]. It has been used in PW analysis to detect total organic matter amenable to GC [45]. However, FID and other non-selective detectors could not overcome the PW matrix issues. Thus, the selective detector, MS, is often required to couple with GC for PW characterization [41].

Besides the advantage of easy sample preparation, a large amount of mass spectrometry database and accessibility are other two reasons that have stimulated the application of GC-MS for VOCs and SVOCs analysis in PW, as discussed in Section 6.1 [20]. Comprehensive two-dimensional GC paired with ToF-MS (GC × GC-ToF-MS) with a higher resolution has also been used to identify a large number of volatile compounds in PW, including geogenic compounds, fluid additives, and potential transformation products [45,61]. GC × GC is a technique that generally separates the analytes by the boiling point on the first column and then by polarity on the second column. It is powerful enough to analyze very complex mixtures. However, very few studies have used it, likely due to high expense, need for qualified operators, and extensive data processing [55].

6.3. Non-Volatile Organic Analysis

Analysis of more polar and non-volatile organic compounds is challenging due to the complexity of the PW matrix of and the lack of knowledge of what compounds may be present in PW, especially for the transformation product analysis. For example, alkyl ethoxylates (AEOs) are usually used as surfactants in HF fluid, but they are rarely detected in PW. Recent studies proved that the AEOs transformed to PEGs through central cleavage of the ethoxylate chain from the alkyl group, making the detection of AEOs difficult without knowing its transformation product [76].

High-performance liquid chromatography–mass spectrometry (HPLC-MS) is a useful tool to analyze non-volatile compounds in PW. HPLC-MS has been used to identify compounds such as glutaraldehyde, amino ethoxylates, and propoxylates [53,69]. However, little research has been conducted to characterize PW or monitor groundwater located near UD sites by using HPLC-MS compared to the use of GC-MS [5]. This could be due to the high instrument cost, lack of libraries for MS data when using ESI-MS, and the complexity of PW matrix [21,60].

Luek et al. [60] reviewed 18 publications analyzing organic compounds in shale gas PW from 2009 to 2016 and found 14 publications used GC-based techniques, and only 4 used LC-based techniques; 1 publication used FT-ICR-MS, and Orbitrap was not reported. Table S4 summarizes 25 peer-reviewed publications analyzing organic compounds in shale gas PW from 2016 to date. In summary, 14 publications used LC-MS, while 13 used GC-based techniques (the overlap is because some publications used both techniques). This trend may be a result of advances in HRMS and ultra-HRMS, in addition to the concerns surrounding undisclosed proprietary chemicals used during HF and their transformation products during well production. Orbitrap (7 publications) and Q-ToF (7 publications) have become the dominant HRMS/MS analyzers because of their high resolution and relatively low price. In comparison, only two publications from the same group used FT-ICR-MS, likely due to its high cost despite the high resolution.

Nontarget analysis has become a more important tool to discover "unknown" chemicals in PW samples using HSMS/MS (Table S4). This approach requires no prior information about the unknown chemicals in PW. The unknown chemicals are defined as chemicals that have not been previously confirmed by reference standards or are not reported on suspects lists (such as in FracFocus). The basic procedure for nontarget analysis is first to collect the mass spectra of unknown chemicals, and data processing techniques are used to assign potential molecular formulas. Chemical structure identification is achieved by database spectra searching (confidence Level 2) or matching the MS/MS spectra and retention time with reference standards (confidence Level 1) [41]. One drawback of nontarget analysis is the possible bias that resulted from sample preparation. Because SPE is the most suitable pretreatment for LC-MS but requires prior knowledge about the analytes to optimize the procedure, more effort is required to analyze PW without losing useful information during comprehensive nontarget analysis.

Sitterley et al. used nontarget analysis and discovered amino-poly (ethylene glycol)s, amino-poly(ethylene glycol) carboxylates, and amino-poly(ethylene glycol) amines in PW samples from HF in the western United States [69]. These compounds were not listed in FracFocus reports and categorized as a proprietary surfactant blend. They first used HPLC-ultrahigh-definition Q-ToF MS for the sample analysis. The measured accurate mass from the total ion chromatogram peak was used to obtain a neutral formula with the MassHunter formula generator. After searching the ChemSpider database for this formula, a polyethylene glycol (PEG) structure containing a primary amine on one end and a hydroxyl group on the other end was given. They also noticed that the mass difference between the major peaks was the calculated exact mass of an ethylene oxide unit ($O-CH_2-CH_2$). Thus, they suspected the peaks were amino-PEGs with ethoxylated chains in the range of $n = 5$–8. The analytical standard (confidence level 1) of $C_{12}H_{27}NO_6$ (amino-PEG6) was obtained to verify their hypothesis. The putative amino-PEG6 in the PW sample and standards were run for MS/MS analysis. The chromatograms for each one has the same retention time and nearly identical MS/MS mass spectra. Kendrick mass defect was used to verify the series of amino-PEGs because compounds that only differ by the addition or subtraction of one or more ethylene oxide units are related by having the same Kendrick mass defect. Other series of compounds were discovered in the same way.

6.4. Three-Dimensional Excitation-Emission Matrix Fluorescence Spectroscopy

The techniques discussed above have similar disadvantages, such as high cost, the requirement of meticulous sample preparation, and the time required to obtain the results.

Quick and effective characterization and quantification of DOM is required to facilitate broad reuse of PW. Three-dimensional fluorescence spectroscopy is an alternative approach to characterize DOM in PW because most organic molecules, such as proteins and bacterial metabolites, have fluorescent emission characteristics. 3D fluorescence produces an excitation-emission matrix (EEM) depending on the chemical structure and functional groups of DOM in the sample. Different groups of organics can be separated based on their intensity or location in the EEMs. 3D fluorescence measurements are quick and comparatively simple, sensitive, and affordable [77].

Riley et al. used 3D EEMs to monitor the DOM changes during PW treatment. They used parallel factor analysis (PARAFAC) to decompose the 3D EEMs into chemically independent groups of chromophore components. Their semi-quantified results were validated by several quantitative analytical techniques, including LC-OCD, LC-HRMS, and GC-MS [42]. Wang et al. also used 3D EEMs with fluorescence regional integration (FRI) to characterize and semi-quantify the DOM in FW and PW from Bakken shale, Barnett shale, and DJ basin [78]. The studies proved that 3D fluorescence could be a powerful and inexpensive tool to comprehensively and continuously monitor the DOM in PW, which is essential when the analysis does not target specific organics. It can also facilitate the early detection of system disruptions and guide researchers to choose proper advanced analytical techniques.

7. Inorganic Analysis

Inorganic constituents in PW are often monitored to preserve and protect the equipment in the field. Sodium and chloride are the dominant ions in PW, and high-salinity water corrodes metal pipes and instruments quickly. Additionally, calcium, magnesium, barium, and strontium can form a scale with carbonate and sulfate to decrease the performance of the whole system [79]. Sulfate in PW can also be reduced to hydrogen sulfide, which can corrode infrastructure and is a safety hazard to workers. Elevated levels of boron, iron, and titanium can cause a series of problems during HF, such as over crosslinking, reduced gel viscosity, and inefficient proppant dispersion [30]. Furthermore, the high concentration of ions, especially sodium and chloride, often obstruct the subsequent analysis, treatment, and reuse of PW.

Conductivity and TDS can provide a relative estimation of ions dissolved in PW, while advanced analytical methods are required to measure the composition of individual ions. To analyze anions in PW, such as chloride, bromide, phosphate, nitrate, and sulfate, ion chromatography (IC) is the preferred analytical technique [5]. EPA has two approved methods for anion determination: method 300.0 and 300.1. Method 300.0 is more suitable for PW because it can be applied to industrial wastewater [75]. Currently, the commercial IC system often uses a conductivity detector. Cantlay et al. expanded the IC performance by using ultraviolet/visible light (UV/VIS) and conductivity detectors in tandem, which increased the selectivity for nitrate, nitrite, and bromide in PW samples [80].

For cation analysis, inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma-mass spectroscopy (ICP-MS) are the preferred methods. They can simultaneously analyze multiple elements in one sample, more convenient than flame atomic absorption (FAA) or graphite furnace atomic absorption (GFAA), which can only analyze one element at a time. Another advantage for ICP-based techniques is that they require minimal sample preparation, often only need filtration, dilution, and addition of acid because the high temperature of an ICP torch can eliminate most of the interferences in the PW matrix [5]. The EPA approved standard methods for ICP-OES and ICP-MS are EPA 200.7 and EPA 200.8/EPA 6020B, respectively [75]. Generally, ICP-MS can provide a detection limit down to parts per trillion (ppt, or ng/L) level in a sample. Cantlay et al. compared the selectivity and sensitivity of ICP-MS and ICP-OES for cation analysis in the high salt matrix of O&G brine from conventional and unconventional wells. The results demonstrated that ICP-MS is better for multi-element analysis at sub-ppb levels;

however, ICP-OES can provide single-digit ppb for most elements. They also found the spectral interferences with ICP-OES were minimal even with the high sodium content as it emits in the high visible range. However, ICP-MS can be susceptible to polyatomic interferences caused by ions consisting of more than one atom or charge, such as $^{40}Ar^{35}Cl$ and $^{40}Ca^{23}Na$ ions affecting ^{75}As signal and $^{40}Ar^{16}O$ and $^{40}Ca^{16}O$ ions affecting the ^{56}Fe signal. Collision/reaction cells have been applied in quadrupole ICP-MS to remove spectral interferences (matrix and argon-based interferences, EPA Method 6020B). Reaction mode uses specific reaction gases to remove known reactive interferences, while helium collision mode with kinetic energy discrimination is universal; it does not need a specific setup for an analyte or a matrix. [81,82]. Despite ICP-OES being less sensitive, it is less expensive and easier to perform, and most metals in PW are abundant enough to be measured by it. Therefore, the choice between the two methods depends on the targeted metal ions and the sample matrix.

Proper sample preparation, such as filtration using 0.22 µm or 0.45 µm filters and dilution, is always required for inorganic ion analysis to ensure more accurate results. SPE using metal affinity resins has been used to detect trace elements in seawater; it can also be applied to PW analysis [83]. In addition, nitric acid is often used to adjust solution pH to below 2 to stabilize the samples for cation analysis. Series of dilution is often necessary to get the result for each ion [80].

Assessing rare earth elements (REEs) concentrations in geothermal water and PWs has become more critical due to their potential as strategic mineral commodities. While several methods exist for REEs analysis, such as laser-induced breakdown spectroscopy (LIBS) and instrumental neutron activation analysis (INAA), ICP-MS is the predominant method used by researchers [84,85]. Currently, there is no EPA method for REEs analysis. However, the U.S. Geological Survey (USGS) Open File Report 02-223, Chapter K details the measurement of REEs in geological materials [86]. Quillinan et al. [87] applied ICP-MS to analyze REEs in PW in the U.S. Two sophisticated sample preparation methods were developed based on the TDS level to eliminate the impact of high salinity and hydrocarbons and preconcentrate the REEs. One approach is suitable for samples with TDS lower than 4.5 g/L, while another procedure is specified for samples with TDS from 4.5 to 300 g/L. There are other methods for specific ion detection, such as an ion-selective electrode. For example, Xu et al. [88] and Almaraz [47] used an iodide double-junction ion-selective electrode to measure iodide concentration in PW.

8. Microbiological Characterization

The characterization and enumeration of the microbial communities in PW are critical for understanding and limiting the impact on corrosion, fouling, and souring issues, thus protecting well infrastructure, minimizing biocide dosage, and supporting PW reuse. Currently, there are no standards regarding the acceptable levels of bacteria in PW [59]. Different methods, both culture-dependent and culture-independent, can be used to measure bacteria, such as plate counting methods, molecular methods, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS) [59]. Plate counting methods are the most commonly used in industry, where the samples are placed on different nutrient agar plates and incubated for a certain amount of time. Differential nutrient media containing specific ingredients are used to distinguish selected species or categories of bacteria by visual observation. Several EPA-approved methods are based on plate counting methods, such as the EPA Method 1600 for Enterococci bacteria in water, EPA Method 1603 for *Escherichia coli (E.coli)* bacteria in water [75]. However, the disadvantage of the plate methods is that only 1% of the microorganisms in nature are able to grow in an artificial environment [89]. Moreover, there is still a lack of developed differential nutrient media and cultivation methods to detect many corrosion-causing microorganisms such as sulfate-reducing bacteria, sulfur-oxidizing bacteria, iron-oxidizing/reducing bacteria, sulfate-reducing archaea, methanogenic archaea, and anaerobic fermenting acid-producing bacteria. Thus, molecular methods are developed to aid the identification of unculturable and slow-growing microorganisms.

Molecular methods include nucleic acid-based techniques, and immunological methods have been applied to study the microorganisms in PW. Nucleic acid-based techniques, such as DNA/RNA sequencing and polymerase chain reaction (PCR), use genetic sequences unique to each microorganism for their identification [90]. PCR can usually be used to amplify the small amount of DNA or RNA in a sample for detection. However, it only works for certain groups of microorganisms with designed primers and is not ideal for identifying the whole microbial community. The new next-generation sequencing (NGS) technology has shown significant advantages in analyzing the microbial community for its unprecedented sequencing depth. It has been applied for investigating microbial structure and functions in various complex environments. This metagenome-based approach could offer a more comprehensive view of the genetic complexity of communities, allowing us to better assess the change of microbial taxonomic diversity and metabolic potential within the bacterial community in water samples [91]. 16S metagenomic sequencing method can be used to identify unknown and unculturable microorganisms; thus, it is widely used to analyze bacteria and archaea in PW [78,90]. Immunological methods are based on the ability of antibodies to recognize specific structures (e.g., proteins or polysaccharides) of biological macromolecules. One example of a commonly used immunological method to evaluate bacteria is the enzyme-linked immunosorbent assay (ELISA), which uses enzymatic reactions to detect the antigen-antibody complex [92]. Recent advances have made it a promising tool that can be applied for target analysis of PW [93].

MALDI-ToF-MS is another powerful tool to analyze microorganisms based on their protein profile [30,63,94,95]. The advantages of this technique are that it can provide metabolic states of the detected cells; it has the potential to directly identify each bacterium in simple mixtures without purification procedures [96]. It can also detect bacteria at the species level. Santos et al. investigated bacteria in groundwater near UD and found that 16S rRNA gene sequencing results for *Klebsiella* sp., *Enterobacter* sp., and *Citrobacter* sp. were not conclusive due to the genetic similarity of those bacterial genera under the same family. In this scenario, the MALDI-TOF showed its advantage and identified the same microorganism as *Klebsiella oxytoca* with a 99.9% match score [97]. However, several disadvantages of this technique have limited its wide application. First, it can only identify culturable microorganisms due to its detection limit. Second, the initial capital cost of this technique is high, although its subsequent analyses are more affordable and faster than nucleic acid techniques. In addition, it requires a microorganism database to identify the bacteria by matching the generated peak lists from MS. Thus, it cannot be used to detect the bacteria with protein spectra not listed in the database, and 16S rRNA gene sequencing is often required to assist the identification process in this situation. The commercial MALDI-ToF-MS microorganism database (such as Shimadzu SARAMIS microorganism database) has been developed primarily for clinical applications and often lack some entries for organisms that are more prevalent in the environment [95]. Hildenbrand et al. used MALDI-ToF-MS to identify the microorganisms present in PW for the first time in 2018. However, they still needed to use 16S rRNA sequencing to identify bacteria that were not successfully identified using MALDI-ToF-MS and to confirm the bacterial identification due to the database problem. With the help of 16S rRNA sequencing, researchers keep adding the protein spectra of those previously unidentified organisms into the MS library for subsequent environmental investigations [30].

In summary, the EPA-approved plate counting methods may be suitable for PW, but they only detect minimal types of bacteria. The 16S rRNA gene sequencing and MALDI-ToF MS are the two most important techniques for identifying bacteria in PW. They are complementary techniques: the 16S rRNA gene sequencing is more reliable in the taxonomic organization, while the MALDI-TOF has better resolving power at the species level [96]. Currently, most of the published literature used 16S rRNA alone or MALDI-ToF MS with 16S rRNA to identify microorganisms in PW or groundwater related to UD.

9. Analysis of Naturally Occurring Radioactive Material (NORM)

Produced water usually contains naturally occurring radioactive material (NORM) because organic-rich shale deposits have inherently higher radioactivity than typical rock formations. Their existence associated with health concern was first realized in the 1980s when unacceptable radiation levels were detected by scrap metal dealers [98,99]. Studies indicate that the concentration of NORM in PW increases with salt content, and the abundant chloride especially enhances the solubility of NORM [100,101]. The commonly found NORM in PW includes uranium (U), thorium (Th), thallium (Tl), and radium (Ra). ^{226}Ra (half-lives of 1500 years) and ^{228}Ra (half-lives of 5.75 years) are the most abundant, which come from the decay of ^{238}U (half-lives of 4.5 billion years) and ^{232}Th (half-lives of 14.5 billion years) [12,102]. The content of ^{226}Ra in the concentrated brine trapped in the Marcellus shale can exceed 10,000 pCi/L, while the standard for drinking water (^{226}Ra and ^{228}Ra) is 5 pCi/L [101]. Radium can accumulate on oilfield equipment through coprecipitation with scale deposits, and the most likely host of radium in the subsurface formation is mineral barite ($BaSO_4$) [98,103]. One study in North Dakota found the NORM in different waste streams from O&G activities, while the scale in equipment had the highest abundance [104]. Another attribute of the PW matrix is the occurrence of sulfate-reducing bacteria, as discussed in Section 8, which increases the solubility of $BaSO_4$, leading to the release of previously encapsulated radium [103].

Evaluating the levels of NORM is critical to protect the person handling PW and the environment. There are three major types of radiation-alpha, beta, and gamma-and the detection methods for NORM usually are based on measuring these types of radiation. For example, ^{226}Ra primarily emits alpha particles, which can be measured directly. ^{228}Ra can be determined by measuring the decay product ^{228}Ac [105]. The EPA has the standard method 903.0 to measure the total soluble alpha-emitting radioisotopes of radium in drinking water. Currently, the EPA-approved methods (900.0, 903.0, 903.1, and 901.1) can only be applied to drinking water, not other water-based samples [75]. One study has proved the EPA Method 903.0 to be inaccurate when applied to PW because of the remarkably high ionic strength and TDS [106,107].

High-purity germanium gamma spectrometer (HPGe-GS) has been proven to be a reliable approach to measure Ra activity in PW. However, this method is limited by the available sample size, long preparation time (21 days to allow ^{228}Ra to reach radioactive secular equilibrium), detector efficiency, and available counting time (6–48 h) [106]. ICP-MS is an effective method for detecting radioactive isotopes compared to the traditional method [108]. Zhang et al. used SPE combined with ICP-MS to analyze ^{226}Ra in PW and compared the result with those obtained from gamma spectroscopy. The study indicated that ICP-MS is a rapid and powerful tool to detect ^{226}Ra with recoveries near 100% from PW samples [105]. Thus, recent studies usually combine HPGe-GS with ICP-MS for PW radioactivity analysis. Rosenblum et al. used HPGe-GS for radionuclide analysis (^{226}Ra, ^{210}Pb, ^{210}Po, ^{234}U, and ^{238}U). The counting time was set to 60,000s for all PW samples unfiltered and acidified with nitric acid (except ^{238}U sample). ICP-MS measured the activities of 238U. Ratios of ^{238}U radioactivity concentrations to ^{234}U radioactivity concentrations were determined by alpha spectrometry using the Eichrom method (ACW02) and uranium-232 as a tracer [28].

Fan et al. [109] compared the HPGe-GS and ICP-MS performance by analyzing ^{226}Ra in PW samples from Antrim and Utica-Collingwood shale (MI) and Marcellus shale (PA). They found that despite the rapid analysis (same day results), ICP-MS measurement of ^{226}Ra did not perform well at high salinity (e.g., 150–230 g/L chloride)/low Ra activity (e.g., <1000 pCi/L) compared to HPGe-GS. However, ICP-MS results had good agreement with HPGe-GS at a lower salinity and higher Ra activity. Moreover, the detection limit of ICP-MS (~1250 pCi/L) is ten times higher than that of the HPGe-GS method. However, because many PW samples fall within the operational salinity range and Ra activity (or with proper sample treatment, dilution, and SPE) of the ICP-MS method, ICP-MS will still be the more efficient method for estimating Ra in PW samples.

10. Summary, Knowledge Gap, and Research Needs

Managing PW, including onsite reuse and beneficial uses outside the oil and gas field after treatment, remains a significant challenge for producers, operators, and regulators due to a lack of complete understanding of the constituents in PW. Risk assessment for PW reuse also heavily relies on knowing the constituents with their concentrations in the water matrix. Therefore, it is crucial to develop a comprehensive understanding of the analytical methods to characterize the known and unknown compounds and to standardize the existing methods suitable for PW analysis with modification and verification.

A multi-tiered analytical approach is proposed to characterize PW quality at all stages and levels of the water cycle from monitoring process performance, modeling potential technology applicability, and evaluating treatment efficiency to assessing environmental and public health risks associated with fit-for-purpose applications and disposal of waste streams. There is a need for developing robust, quick, efficient, accurate, sensitive, and cost-effective analytical methods for characterization of important produced water constituents for screening, treatment process monitoring, pre- and post-treatment quality assurance, application monitoring, and regulatory compliance. Both rapid testing techniques to support process quality assurance (QA) and advanced analytical methods for target and nontarget chemical analysis are required to manage, dispose of, treat, and reuse PW properly. Reliable, accurate, and robust in-line sensors should be developed as Tier 1 analysis of complex produced water chemistry under a harsh environment. Advanced software tools, machine learning, and connected digital systems are also needed to enable data processing, failure analysis, predicting performance, and operation control. Tier 1 analytical results will trigger and guide Tiers 2 to 4 characterization analysis. Tiers 2 to 4 focus on detailed characterization, routine monitoring, and Tier 1 data verification.

Current EPA standard methods are developed for drinking water, municipal, and industrial wastewater. Their application to characterizing PW samples needs to be evaluated. The EPA methods for bulk measurements can be suitable for PW samples with minimal revision; the methods for inorganic measurements can be suitable for PW samples if the interference of high TDS is addressed (e.g., series dilution). For NORM and biological analysis, the current EPA methods will not be sufficient. Sample preparation and long measuring time are two major problems that need to be addressed. Further, the prevalent challenge for PW is the analysis of organics, especially for non-volatile compounds and unknown chemicals. GC/MS-based EPA methods with modification, such as intense sample preparation, may be suitable to analyze VOCs and SVOCs in PW, especially with the help of GC-(EI)-MS database and good reproducibility of GC-(EI)-MS. For non-volatile analysis, LC-HRMS/MS will play a crucial role in identifying unknown compounds in PW from additives or transformation products and quantifying the known compounds. Multi-step sample preparation would tremendously assist the analysis of non-VOCs. However, because of the extremely complex matrix of PW and the limitation of the current LC-HRMS/MS technique, it is still difficult to monitor all the organics in the PW and measure their concentrations to assess the potential risks. Complete current MS database or construct a designated database for PW would significantly assist non-VOCs identification and quantification.

The review results are illustrated in Figure 4, summarizing the proposed approaches for analyzing chemical constituents in PW, including sampling and preservation, sample preparation and pretreatment, and analytical techniques. Table 4 summarizes the standard analytical methods, methods used in commercial labs, and advanced characterization research methods for targeted and unknown compounds. Currently, there is no EPA-approved method for PW samples. EPA-approved methods target known chemicals. The unknown composites in PW require nontargeted analysis, especially for organic compounds. More research is needed to develop these proposed approaches to meet the EPA requirements for regulatory purposes.

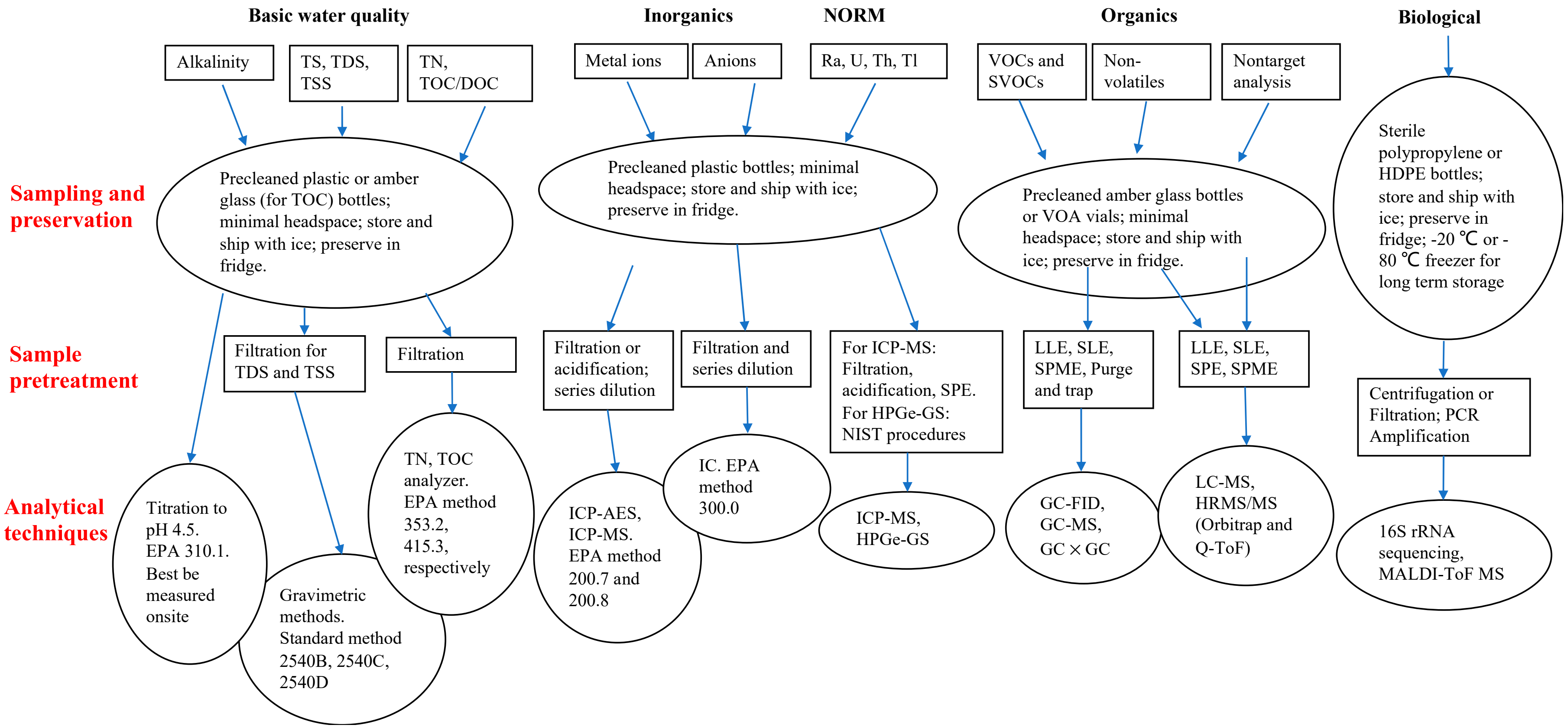

Figure 4. Proposed approaches for analysis of chemical constituents in flowback and produced water.

Table 4. Summary of standard analytical methods and methods used in commercial labs, and advanced characterization research methods for targeted and unknown compounds.

Analytes	EPA-Approved Methods (Water Matrix)	Suitable for PW Analysis?
Basic water quality		
Alkalinity	EPA Method 310.1 and 310.2 (Drinking, surface, and saline waters; domestic and industrial wastes)	EPA Method 310.1 is suitable for PW.
TS	Standard method 2540B (Drinking, surface, and saline waters; domestic and industrial wastewaters)	Yes, range up to 20,000 mg/L
TDS	Standard method 2540C (Drinking, surface, and saline waters; domestic and industrial wastewaters)	Yes, range up to 20,000 mg/L
TSS	Standard method 2540D (Drinking, surface, and saline waters; domestic and industrial wastewaters)	Yes, range up to 20,000 mg/L
TN	EPA Method 353.2: Inorganic nitrite and nitrate; EPA method 351.2 and 351.4: organic nitrogen and ammonia (drinking, surface, and saline waters; domestic and industrial wastes)	Yes, with proper sample preparation
TOC/DOC	EPA Method 415.3 or Standard methods 5310C (Source waters and drinking water)	Yes, with proper sample preparation
pH	EPA 150.1 (Drinking, surface, and saline waters; domestic and industrial wastes and acid rain)	Yes, with proper sample preparation
Inorganic		
Metal ions	EPA 200.7: ICP-AES, EPA 200.8/6020 B: ICP-MS (Drinking, surface, and groundwater; wastewaters, sludges, and solid samples)	EPA methods can be used for PW with a series of dilutions to eliminate the impact of high Na$^+$ concentration. ICP-AES and ICP-OES are reliable approaches.
Anions	EPA 300.0 (drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids); EPA 300.1 (reagent water, surface water, groundwater, finished drinking water)	EPA 300.0 is suitable for PW with a series of dilutions to eliminate the impact of high Cl$^-$ concentration. IC is a reliable approach.
Organic		
Non-Pesticide (120 parameters)	EPA 551, 601–625, 632, 1613B, etc. (drinking, ambient water, wastewater, sediment)	EPA methods based on GC may be suitable to analyze VOCs and SVOCs in PW with proper sample pretreatment, such as purge and trap, LLE, SPE, or SPME. However, the number of compounds is limited.
Pesticide (70 parameters)	EPA 553, 605, 610, etc. (drinking, ambient water, wastewater, sediment)	With proper sample pretreatment, such as LLE, SPE, or SPME, EPA methods based on LC may be suitable to analyze non-volatiles compounds in FPW. However, LC-HRMS/MS (Orbitrap and Q-ToF) would be more reliable approaches.
Nontarget analysis	No methods.	Nontarget analysis using HRMS/MS (confidence Levels 1 and 2) will be required to identify the unknown compounds in PW.
Biological Bacterial	EPA 1600, 1603, 1622, 1680, etc. (Wastewater and Sewage sludge, ambient water)	EPA methods detect limited types of bacteria. 16S rRNA sequencing and MALDI-ToF MS are reliable approaches for FPW.
NORM Ra, U, Th, Tl	EPA 900.0, 901.1, 903.0, 903.1. (Drinking water)	EPA methods cannot be used for PW. HPGe-GS (lower MDL and more accurate) and ICP-MS (more efficient) are reliable approaches.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4441/13/2/183/s1, Figure S1: Temporal variation of PW qualities in Marcellus shale, PA, two well sites; and Niobrara formation, CO, two well sites. Table S1:Comparison of general physicochemical parameters of PW in primary UD plays in minimum-maximum/mean values; Table S2: Analyte containers, preservation, and holding times; Table S3: SPE cartridges used for organic extraction; Table S4: Summary of the recent studies analyzing organic compounds in PW.

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Nomenclature

AEOs	Alkyl ethoxylates
APCI	Atmospheric pressure chemical ionization
ASE	Accelerated solvent extraction
AST	Above surface storage tank
BOD	Biochemical oxygen demand
BSFTA	N, O-bis(trimethylsilyl)trifluoroacetamide
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CI	Chemical ionization
COD	Chemical oxygen demand
DCM	Dichloromethane
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EI	Electron ionization
EPA	Environmental Protection Agency
ESI	Electrospray ionization
FEEMs	Fluorescence excitation-emission matrix
FID	Flame ionization detector
FPSE	Fabric phase sorptive extraction
FT-ICR-MS	Fourier-transform ion cyclotron resonance mass spectrometry
FW	Flowback water
GC	Gas chromatography
GC-FID	Gas chromatography coupled with flame ionization detector
GC-MS	Gas chromatography-mass spectrometry
GC-TCD	Gas chromatography coupled with thermal conductivity detector
HDPE	High-density polyethylene
HF	Hydraulic fracturing
HPGe-GS	High-purity germanium gamma spectrometer
HPLC	High performance liquid chromatography
HPLC-MS	High performance liquid chromatography -mass spectroscopy
HPLC-UV	High performance liquid chromatography coupled with ultraviolet diode array detector
HRMS	High-resolution mass spectrometry
HSGC	Headspace gas chromatography
IC	Ion chromatography
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
ICP-MS	Inductively coupled plasma-mass spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
LC	Liquid chromatography
LC-MS	liquid chromatography-mass spectroscopy
LC-OCD	liquid chromatography coupled with organic carbon detection
LC-UV	liquid chromatography coupled with UV-diode array detector
LEAF	Leaching environmental assessment framework
LLE	Liquid-liquid extraction
MALDI	Matrix-assisted laser desorption/ionization
MDL	Minimum detection limit
MS	Mass spectroscopy
MS/MS	Tandem mass spectrometry
NORM	Naturally occurring radioactive material
O&G	Oil and gas
ORP	Oxidation-reduction potential
PAHs	Polycyclic aromatic hydrocarbons
PEGs	Polyethylene glycols
PTFE	Polytetrafluoroethylene
PW	Produced water
Q	Quadrupole mass analyzer
REEs	Rare earth elements
SEM/EDX	Scanning electron microscopy/energy-dispersive X-ray spectroscopy
SI	Supporting Information
SLE	Solid-liquid extraction
SPE	Solid-phase extraction
SPLP	Synthetic precipitation leaching procedure
SPME	Solid-phase microextraction
SVOCs	Semi-volatile organic compounds
SWD	Salt water disposal
TCLP	Toxicity characteristic leaching procedure;
TDS	Total dissolved solids
TN	Total nitrogen
TOC	Total organic carbon
ToF	Time of flight mass analyzer
TPH	Total petroleum hydrocarbons
TSS	Total suspended solids
UD	Unconventional oil and gas development
UIC	Underground injection control
VOA	Volatile organic analysis
VOCs	Volatile organic compounds
XRD	X-ray diffraction

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