

A critical review of analytical methods for comprehensive characterization of produced water

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1. Produced Water Quality and Temporal Variability in Different Basins

The United States produces large volumes of produced water (PW) from unconventional oil and gas development (UD). 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) [1]. Table S1 summarizes the general physicochemical parameters of PW quality from primary UD plays in the U.S. Fig. S1 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 total dissolved solids (TDS) concentrations than flowback water (FW). However, FW can have higher organics due to organic additives in fracturing fluid [2-4].

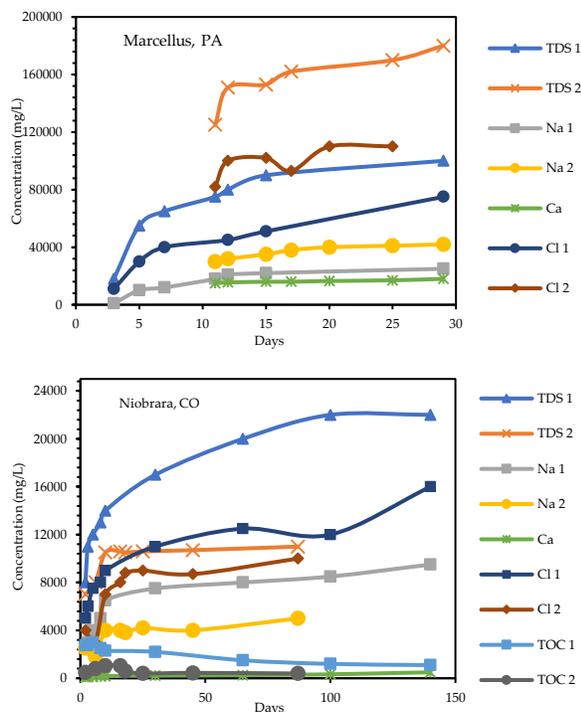


Fig. S1. Temporal variation of PW qualities in Marcellus shale, PA, two well sites [5]; and Niobrara formation, CO, two well sites [3,6].

Table S1. Comparison of general physicochemical parameters of PW in primary UD plays in minimum-maximum/mean values

	Anadarko	Bakken	Barnett	Eagle Ford	Marcellus	Niobrara	Permian
TDS (g/L)	8.9-52.6/ 15.3	5.2-470.3/ 229.2	1.0-398.0/ 199.5	16.9-206.7/ 61.3	1.5-394.6/ 162.1	3.9-109/ 40.3	1.2-430.4/ 147.5
TSS (mg/L)	n/a	3180-7,500	37-6,600	160-1,559	2-7,600	80-1,297	6,850- 21,820
pH	n/a	5.0-6.9/6.0	6.5-8	4.3-8.9	5.1-8.4/6.6	6.5-7.4	6.2-7.5
DOC (mg/L)	n/a	19-225/ 70	5.5-131	248.7-1,100	3.4-5,960	47-2,170	63.5-145.7
Alkalinity (CaCO ₃ , mg/L)	n/a	55-2,000	29-1630	200-2,000	6.1-1,100	70-1,070	118-2,674
Na (mg/L)	3,216- 18,297/ 5,570	12,271- 118,760/ 72,299	278-28,200	5,311-60,106/ 18,481	3,465- 81,590/ 33,545	1,336- 41,778/ 15,389	316- 134,652/ 51,520
Mg (mg/L)	6.3-411/ 29	118-9,805/ 1,181	2-757	34-1,772/ 293	33-3,427/ 1,190	4-170/ 59	6-18,145/ 1,311
Ca (mg/L)	20-1,501/ 84	18-132,687/ 13,520	13-6,730	223-17,072/ 3,330	349-30,736/ 12,247	19-760/ 350	26-46,500/ 6,627
Ba (mg/L)	0.1-39/ 5	0.001-1,400/ 67	0.05-17.9	1.6-1,216/ 37	0.1-22,400/ 2,495	n/a	1.1-1,136/ 167
K (mg/L)	8.6-48/ 28	30-8,526/ 4,386	4-750	43-3,421/ 295	20-1,910/ 395	10-100/ 45	17-14,649/ 841
Cl (mg/L)	4,500- 31,667/ 8,172	21,728- 310,561/ 142,816	6,500- 72,400	9,182- 123,579/ 35,926	5,935- 160,545/ 80,764	1,473- 66,000/ 24,093	1,405- 216,575/ 95,820
SO ₄ (mg/L)	3.4-206/ 94	27-6,258/ 514	120-1,260	6.4-346/ 92	0.6-199/ 46	0.5-306/ 46	2-7,851/ 1,024
HCO ₃ (mg/L)	537-1,562/ 1,003	1.9-7,355/ 238	145-994	537-537/ 537	n/a	171-1,783/ 619	7-6,346/ 440
Total Ra (pCi/L)	n/a	786-1,722/ 1,225	n/a	137-558/ 312	0.2-18,045/ 3,250	n/a	58-1,542/ 591

Note: data compiled from 2020 Scanlon et al. [7], 2020 Rodriguez et al. [8], 2019 Chang et al. [9], 2018 Lipus et al. [10]. n/a: data not available. TSS: total suspended solids.

2. Field Sampling and Preservation

2.1. 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. 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.

Sampling equipment and preservation techniques are important for environmental samples. The EPA approved analytical methods for drinking water or wastewater have detailed instructions on sample collection, preservation, and storage. For example, the EPA Method 625 (for organic analysis) states that “samples must be collected in glass containers”, “All samples must be iced or refrigerated at 4 °C from the time of collection until extraction”, “If residual chlorine is present, add 80 mg sodium thiosulfate per liter of sample”. Thus, the sampling equipment and preservation techniques used for PW samples are even more crucial due to their extremely complex matrices and high oxidation potential of certain constituents (e.g., iron). The target analytes can be easily adsorbed to the container or degraded during conveyance or storage. For waste and wastewater matrices, the EPA’s SW-846 compendium is a more suitable candidate for PW sample preparation and analysis. A major concern for PW samples is the biodegradation of numerous organic compounds. Acids or sodium azide are often used to preserve PW samples [11]. Immediate transfer of hydrophobic analytes out of the aqueous phase in the field using a water-immiscible organic solvent is another method to minimize biodegradation. Another concern is some of the highly reactive HF additives and metal ions [12]. To detect those highly reactive targets in PW, their transformation/degradation has to be minimized at the time of sampling by adding chemical preservatives, extracting into an organic solvent, or onsite filtration. Targeting the more stable intermediates from transformation during analysis is also a good approach if the parent compounds are known. However, for those preservation methods, their compatibility with the fundamental analysis must be considered before application because they may suit one target analyte but not the others [13].

Lipus et al. [14] used 16S rRNA sequencing to monitor the changes in microbial community composition in PW at different sample storage conditions. Their results suggested an ideal handling method for microbiology analysis would be filtering the sample on-site and preserving the filters with chemical preservatives (such as TRIZOL). If on-site sample processing is not possible, the best way to maintain the original microbial communities would include collecting samples in sterile bottles in the field and placing them on ice as soon as possible, but at least within 24 h, followed by shipping the samples on ice over 2-3 days. Furthermore, samples should be stored at the -20 °C or -80 °C for long-term storage.

The widely used containers for PW samples include sterile or precleaned photo resistant glass bottle (e.g., amber glass bottle) and clean plastic bottles (e.g., high-density polyethylene (HDPE) and polytetrafluoroethylene (PTFE)). They are suitable for almost all samples with several particular cases. The biological sample requires sterile HDPE or polypropylene bottles, while the boron and silica sample requires plastic, PTFE, or quartz containers. Minimal headspace is necessary during sampling to minimize partitioning into the gaseous phase. The collected sample should be stored with ice and sent to the lab for analysis as soon as possible. If immediate analysis cannot be performed, samples should be stored in a refrigerator and analyzed as soon as possible. The following preservation methods are recommended to enhance the accuracy of the results. To determine the dissolved inorganic elements, samples must be filtered through a 0.45 µm membrane filter at the time of collection or as soon as practicable. To determine the total recoverable inorganic elements, samples are not filtered but acidified with trace metal grade nitric acid to pH < 2. Acid is often used to preserve some biocides, and chloroform is added for anions. Organics should be preserved in a fridge (2 - 6 °C) or - 20 °C, and should not be stored longer than two weeks before analysis [15].

For quality assessment, duplicate samples are collected to evaluate precision, including variability in sample collection, handling, preparation, and analysis. Sample blanks are also required to increase analysis confidence by eliminating possible contamination during sample collection, conveyance, or preparation [16], such as analytical blanks [17,18], field blanks [18,19], trip blanks [6], equipment blanks, laboratory blanks [18], and storage blanks [17].

Table S2. Analyte containers, preservation, and holding times

Analyte	Method (Technique)	Sample Container ¹	On-Site Preservation	Holding Time
Inorganic and Wet Chemistry				
Alkalinity	SM 2320 B-1997 (Titration)	250 mL - Plastic	Cool to $\leq 6^{\circ}\text{C}$	14 Days ¹
Ammonia	EPA 350.1 (Colorimetric)	250 mL - Plastic	H ₂ SO ₄ until pH < 2, Cool to $\leq 6^{\circ}\text{C}$	28 Days
Biochemical Oxygen Demand (BOD ₅)	SM 5210 B-2001 (Titrimetric)	1000 mL - Plastic	Cool to $\leq 6^{\circ}\text{C}$	48 Hours
Chemical Oxygen Demand (COD)	EPA 410.4 (Spectrophotometric)	500 mL - Plastic	H ₂ SO ₄ until pH < 2, Cool to $\leq 6^{\circ}\text{C}$	28 Days
Chlorine, Total Residual	SM 4500 Cl- G	250 mL - Plastic	Not required	15 Minutes
Dissolved Oxygen	EPA 360.2	500 mL - Glass	Not required	15 Minutes
Fluoride, Chloride, Nitrite, Ortho-Phosphate-p, Bromide, Nitrate, Sulfate Bromate, Chlorite, Chlorate	EPA 300.0 (Ion Chromatography)	500 mL - Plastic	Cool to $\leq 6^{\circ}\text{C}$	28 Days except NO ₂ , NO ₃ , Ortho-P 48 Hours
Fluoride, Chloride, Nitrite, Ortho-Phosphate, Bromide, Nitrate, Sulfate	ASTM D4327 (Suppressed Ion Chromatography)	500 mL - Plastic	Cool to $\leq 6^{\circ}\text{C}$	28 Days except NO ₂ , NO ₃ , Ortho-P 48 Hours
Hardness	SM 2340B	250 mL - Plastic	HNO ₃ until pH is < 2, Cool to $\leq 6^{\circ}\text{C}$	6 Months
Iodide	EPA 345.1	250 mL - Plastic	Cool to $\leq 6^{\circ}\text{C}$	24 Hours
Methylene Blue Active Substances (Surfactants, anionic)	EPA 425.1	250 mL - Plastic	Cool to $\leq 6^{\circ}\text{C}$	48 Hours
N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM)	EPA 1664A (Gravimetric)	1 L - Wide-Mouth Glass	HCl or H ₂ SO ₄ until pH < 2, Cool to $\leq 6^{\circ}\text{C}$	28 Days

Nitrogen, Ammonia	SM 4500 NH3-B,C	500 mL - Plastic	H ₂ SO ₄ until pH < 2, Cool to ≤ 6°C	28 Days
Nitrogen, Total Kjeldahl	SM 4500 Norg B,C SM 4500 NH3-C	500 mL - Plastic	H ₂ SO ₄ until pH < 2, Cool to ≤ 6°C	28 Days
Phenolics	EPA 420.4	1 L - Glass	H ₂ SO ₄ until pH < 2, Cool to ≤ 6°C	28 Days
Phosphorous, Total	ASTM D515	500 mL - Plastic	H ₂ SO ₄ until pH < 2, Cool to ≤ 6°C	28 Days
Salinity	SM 2520	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Silica	EPA 200.7/6010 D	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Specific Conductance	SM 2510 B-1997 (Conductivity Meter)	100 mL - Plastic	Cool to ≤ 6°C	28 Days
Sulfate	300.0/375.4	500 mL - Plastic	Cool to ≤ 6°C	28 Days
Sulfide	SM 4500-S D	500 mL - Plastic	Cool to ≤ 6°C Zn Acetate & NaOH to pH > 9	7 Days
Sulfite	SM 4500 SO3-B	100 mL - Plastic	Not required	15 Minutes
Total Dissolved Solids (TDS)	SM 2540 C-1997 (Gravimetric)	250 mL - Plastic	Cool to ≤ 6°C	7 Days
Total Hardness	SM 2340 C-1997 (Titrimetric)	250 mL - Plastic	HNO ₃ or H ₂ SO ₄ until pH is < 2, Cool to ≤ 6°C	6 Months
Total Organic Carbon (TOC)	EPA 415.1 SM 5310 B-2000 (Combustion)	250 mL – Amber Glass	H ₂ SO ₄ or H ₃ PO ₄ until pH < 2, Cool to ≤ 6°C	28 Days
Total Suspended Solids (TSS)	SM 2540 D-1997 (Gravimetric)	1000 mL - Plastic	Cool to ≤ 6°C	7 Days
Turbidity	EPA 180.1	100 mL - Plastic	Cool to ≤ 6°C	28 Hours
Metals				
Trace elements (Total)	EPA 200.7 (ICP), EPA 200.8/EPA 6020B(ICPMS)	500 mL - Plastic	HNO ₃ until pH is < 2	6 Months

Trace elements (Dissolved)	EPA 200.7 (ICP), EPA 200.8/EPA 6020B(ICPMS)	500 mL - Plastic	0.45 μm filtration in 15 minutes, HNO_3 until pH is < 2	6 Months
Mercury	EPA 245.1 or 245.2 (Cold Vapor Atomic Absorption)	500 mL - Plastic	HNO_3 until pH is < 2	28 Days
Hexavalent Chromium	SM 3500 -Cr B-2009 (Colorimetric)/ EPA 7199	250 mL - Plastic	Cool to $\leq 6^\circ\text{C}$	24 Hours
Organics				
Alcohols	EPA 8260C, 8270D, and 8015C (GC/MS)	40-mL VOA vials	HCl until pH < 2, Cool to $\leq 6^\circ\text{C}$	14 Days
Aldehydes	EPA 8315(HPLC)	250 mL - Amber Glass	Cool to $\leq 6^\circ\text{C}$	3 Days
Diesel Range	EPA 3520C (sample preparation) EPA 8015C (analysis) (GC)	1-L - Amber Glass	Cool to $\leq 6^\circ\text{C}$	7 Days
Gasoline Range	EPA 5030B (sample preparation) EPA 8015C (analysis) (GC)	40-mL VOA vials	Cool to $\leq 6^\circ\text{C}$	7 Days
GCMS Purgeables	EPA 524.2	40-mL VOA vials	Ascorbic acid and HCl until pH < 2, Cool to $\leq 6^\circ\text{C}$	14 Days
GCMS Purgeables	EPA 624/8260C	40-mL VOA vials	HCl until pH < 2, Cool to $\leq 6^\circ\text{C}$	14 Days
Haloacetic Acids	EPA 552.2	250 mL - Amber Glass	Cool to $\leq 6^\circ\text{C}$, NH_4Cl	14 Days
Herbicides	EPA 8151A (GC)	1-L - Amber Glass	Cool to $\leq 6^\circ\text{C}$	7 Days
Oil & Grease	EPA 1664B (Extraction and Gravimetry)	1-L Amber Glass	HCl or H_2SO_4 until pH < 2, Cool to $\leq 6^\circ\text{C}$	28 Days
Pesticides	EPA 608/8081B (GC)	1-L Amber Glass	Cool to $\leq 6^\circ\text{C}$	7 Days
Semivolatile Organic Compounds + Tentative Identified compounds	EPA 3520C/8270D (GC /MS)	1-L - Amber Glass	Cool to $\leq 6^\circ\text{C}$	7 Days

Semivolatile Organic Compounds + Tentative Identified compounds	EPA 625/8270D (GC)	1-L - Glass	Cool to $\leq 6^{\circ}\text{C}$, Add $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of residual chlorine	7 Days
Total Petroleum Hydrocarbons	EPA 1664B (Extraction and Gravimetry)	1-L Amber Glass	HCl or H_2SO_4 until pH < 2, Cool to $\leq 6^{\circ}\text{C}$	28 Days
Volatile Organic Compounds + Tentative Identified compounds	EPA 5030 or EPA 5035/8260C (GC/MS)	40-mL VOA vials	HCl until pH < 2, Cool to $\leq 6^{\circ}\text{C}$	14 Days
Volatile Organic Compounds + Tentative Identified compounds	EPA 624.1 (GC /MS)	40-mL VOA vials	HCl until pH < 2, Cool to $\leq 6^{\circ}\text{C}$, Add $\text{Na}_2\text{S}_2\text{O}_3$ (a few crystals) in the presence of residual chlorine	14 Days
Radioactive				
Total Radium 226 (Liquid Samples)	EPA 903.1 (Radon Emanation)	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Total Radium 228 (Liquid Samples)	EPA 904.0 (Radiochemical/Precipitation)	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Total Radium 226 and 228 (Solid Samples)	EPA 901.1 (Gamma Spectroscopy)	215 grams - Wide-Mouth Plastic	None	6 Months
Gross Alpha/Beta (Liquid Samples)	EPA 900.0 (Evaporation)	500 mL – Wide-Mouth Plastic	HNO_3 until pH is < 2	6 Months
Gross Alpha/Beta (Solid Samples)	EPA 900.0 (Evaporation)	30 grams - Wide-Mouth Plastic	None	6 Months
Microbiological				
Coliform, Fecal	SM 9222D	250 mL - Sterile Plastic	Cool to $\leq 6^{\circ}\text{C}$	8 Hours
Coliform, Fecal Strep	SM 9230A/B	250 mL - Sterile Plastic	Cool to $\leq 6^{\circ}\text{C}$	6 Hours
Coliform, Total	EPA 1603	250 mL - Sterile Plastic	Cool to $\leq 6^{\circ}\text{C}$	8 Hours
Coliform, E.Coli	EPA 1603	250 mL - Sterile Plastic	Cool to $\leq 6^{\circ}\text{C}$	8 Hours
Enterococci	EPA 1600	250 mL - Sterile Plastic	Cool to $\leq 6^{\circ}\text{C}$	8 Hours

Heterotrophic Plate Count	SM 9215B	250 mL - Sterile Plastic	Cool to $\leq 6^{\circ}\text{C}$	8 Hours
Whole Effluent Toxicity (WET)				
Acute Nonvertebrate	<i>Ceriodaphnia dubia</i> EPA 2002.0	4-L - Plastic Cubitainer	Cool to $\leq 6^{\circ}\text{C}$	36 Hours
Acute Vertebrate	<i>Pimephales promelas</i> EPA 2000.0	4-L - Plastic Cubitainer	Cool to $\leq 6^{\circ}\text{C}$	36 Hours
Chronic Nonvertebrate	<i>Ceriodaphnia dubia</i> EPA 1002.0	4-L - Plastic Cubitainer	Cool to $\leq 6^{\circ}\text{C}$	36 Hours
Chronic Vertebrate	<i>Pimephales promelas</i> EPA 1000.0	4-L - Plastic Cubitainer	Cool to $\leq 6^{\circ}\text{C}$	36 Hours

1. Alkalinity: 14 days holding time for treated samples and should be analyzed as soon as possible for untreated samples.

2.2. Sample preparation

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.

2.2.1 Dilution, filtration, and centrifugation

Dilution is a useful way to address the sample matrix, making it more suitable for the analytical instrument and adjusting the concentration of analytes into the calibration range. Filtration and centrifugation are two simple sample preparation methods. They both remove particulate materials in PW to make samples compatible with analytical methods and protect instruments, such as to prevent clogging and high backpressure for ion chromatography (IC) and liquid chromatography (LC) columns [20]. However, filtration and centrifugation do not concentrate the sample or change the dissolved fraction of the sample matrix, which may be required when analyzing PW, especially when targeting trace amounts of organic analytes. Thus, these methods usually can only be applied to bulk and inorganic measurements and need to be coupled with other pretreatment methods for organic sample analysis [21]. Another important consideration for these methods is their bias toward chemical constituents adsorbed to the suspended solids in the matrix, which are often removed during the filtration process [13]. Thus, the filtered solids are sometimes collected and treated (e.g., acid digested) to analyze the PW sample comprehensively [17].

2.2.2 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 [6,22,23]. Table S3 summarizes the SPE cartridges used in literature for organic analysis.

Table S3. SPE cartridges used for organic extraction

Ref.	SPE, analytes, and analytical method	Ref.	SPE, analytes, and analytical method
2019 Akyon. [20]	Supelco, Super Select HLB cartridges (200 mg/6 mL), surfactants, LC-MS. Recoveries: less than 100%.	2018 Oetjen. [6]	PerkinElmer, Supra-Clean C18-S cartridge, PAHs, GC-MS.
2019 Sorensen. [24]	Agilent, Bond Elut SI Silica SPE columns (500 mg), non-target, LC-MS.	2018 Riley. [25]	Thermo Scientific Dionex SolEx C18 cartridges (500 mg/6 mL), PAHs, GC-MS.
2019 McAdams. [26]	Waters, SEP Pak C-18 cartridges, surfactants (alkyl ethoxylates and polyethylene glycols) LC-MS.	2017 He. [27]	Waters, Silica cartridges (1g/6 ml), PAHs, GC-MS.
2018 He. [17]	Waters, silica cartridge (1g/6 ml), non-target, LC-MS.	2017 Luek. [18]	Agilent, Bond Elut PPL SPE cartridges (1g/3 mL), halogenated organics, MS. Recoveries: 0.04%- 48%
2018 Sitterley. [28]	Waters, Oasis HLB cartridge, amino-poly (ethylene glycol)s, amino-PEG- carboxylates, and amino-PEG amines LC-MS.	2016 Regnery. [22]	Thermo Scientific Dionex SolEx C18 cartridges (500 mg/6 mL), GC-MS. Recoveries: 38–120% for linear aliphatic hydrocarbons and 84–116% for PAH.

3. 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 [16]. 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 [29]. 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].

Alkalinity in PW is caused by carbonate and bicarbonate ions, which affect the pH of the solution and have the potential to induce scaling with cations (e.g., Ca^{2+}) present in the solution [31]. Alkalinity can be measured by titration using the EPA Method 310.1 and the colorimetric testing EPA Method 310.2. The EPA Method 310.1 is more suitable for PW measurement because PWs usually present in yellow color, which can affect the accuracy of colorimetric testing, and using a pH meter to titrate the sample to endpoint pH 4.5 would be more accurate [32,33]. There are many different alkalinity measurement test kits available in the market that are suitable for onsite testing.

Solids refer to the substances suspended or dissolved in PW. Total solids (TS) includes TSS and TDS. TSS are particles mainly comprised of formation sands and clays, proppants, and corrosion byproducts.

TDS are primarily charged particles (major cations and anions). TDS levels can vary considerably in a given region. For example, PW in Bakken shale varies from 1,800 to 350,000 mg/L TDS [9]. There are two principal methods for measuring TDS: gravimetric analysis and conductivity. The gravimetric method is more accurate than the conductivity method, while the latter is more convenient. Dilution is often required for the conductivity method to yield accurate results within the instrument measurement range. Currently, TS, TSS, and TDS are often measured by the Standard Methods 2540 A-F (gravimetric methods, range up to 20,000 mg/L) approved by the EPA to analyze solids residue from domestic and industrial wastewater [34]. TS is measured by evaporating a well-mixed sample in a weighed dish and dried to constant weight in an oven at 103 to 105 °C. The increase in dish weight represents the TS (method 2540B). TSS and TDS can be measured at the same time. A well-mixed sample is first filtered through a weighed standard glass-fiber filter. The residue retained on the filter is dried to a constant weight at 103 to 105 °C; the filter weight increase represents the TSS (method 2540D). TDS is obtained by evaporating the filtrate in a weighed dish and dried to constant weight at 180 °C; the dish weight increase represents the TDS (method 2540C) [32,35].

TOC provides the concentration of organic carbon in water. It is a more convenient and accurate measurement to perform in the lab than biochemical oxygen demand (BOD) or chemical oxygen demand (COD) methods. The EPA Method 415.3 or the Standard Method 5310C is usually used to measure TOC. Samples are first acidified by HCl, H₃PO₄, or H₂SO₄ to pH < 2, to remove the inorganic carbon (carbonate and bicarbonate). The organic carbon is then oxidized to carbon dioxide by combustion or chemical oxidation, which is then detected by a conductivity detector or a nondispersive infrared (NDIR) detector [36]. DOC is another commonly measured parameter representing the dissolved (filtered) organic compounds in water. The procedure requires the sample to be filtered by a 0.45 µm filter before analysis by a TOC analyzer (e.g., Shimadzu TOC analyzer TOC-L or TOC-V series) [37]. Dilution sometimes is needed when the concentration of DOC exceeds the optimum range of the instrument [38].

TN is the sum of the inorganic nitrogen, organic nitrogen, and ammonia. Inorganic nitrite and nitrate are analyzed using the EPA Method 353.2: nitrate in a filtered sample is reduced to nitrite, then all the nitrite is measured colorimetrically. The sum of organic nitrogen and ammonia can be analyzed using EPA Methods 351.2 and EPA-NERL 351.4. The sample is digested to convert total Kjeldahl nitrogen (total nitrogen in organic substances and inorganic ammonia/ammonium) into ammonia. Then the concentration of ammonia is measured using an ion-selective electrode [32,33]. Another method (ASTM D8083) to determine TN is to convert all nitrogen compounds to NO, followed by photoelectric measurement of radiation emitted when NO₂ relaxes [39].

These methods are easy to perform if the samples are correctly prepared. Dilution is usually a convenient way to avoid interferences because these bulk parameters do not measure constituents at trace levels. Table S1 includes some measurement results of the typical water quality parameters from different PW sources.

4. Organic Analysis

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 2 publications from the same group used FT-ICR-MS, likely due to its high cost despite the high resolution.

Table S4. Summary of the recent studies analyzing organic compounds in PW

Ref.	Basin/formation, sample	Target analytes	Pretreatment methods	Analytical methods	Quantified
2020 Almaraz. [38]	DJ basin (CO), PW	Iodinated organic compounds (5 volatile IOCs) during biological treatment of FPW	IOCs are treated by polydimethylsiloxane/divinyl benzene (PDMS/DVB) fiber	HS-SPME-GC-MS(QQQ); Iodide double-junction ion-selective electrode	YES
2019 Akyon. [20]	Utica and Bakken shales, PW	Total, dissolved organic carbon during biological treatment	LLE (DCM) for GC-MS; SPE for LC-MS. Super Select HLB cartridges (200 mg/6 mL, Supelco)	GC-MS (Q) for SVOCs; LC-MS (Q-ToF) for surfactants	YES
2019 Sorensen. [24]	Norwegian North Sea oil field, PW	Total organic extracts (TOEs); Nontarget analysis	LLE (DCM) for TOEs; Silica SPE cartridge (Agilent Bond Elut SI) Some samples derivatized with BSFTA.	GC-FID for GC-amenable compounds; GC-MS (Q) for decalins, PAHs, alkylated PAHs and C ₀₋₉ phenols; GC X GC-MS (ToF) and LC-HRMS (Orbitrap) for non-target analysis	YES
2019 Sun. [40]	Duvernay Formation (Canada), FPW over 30 days of flowback Bakken shale (ND), FW;	Nontarget profiling. Identified 7 series of homologues composed of ethylene oxide and 2 series of alkyl ethoxylates	LLE (DCM)	HPLC-HRMS (Orbitrap), ESI both positive and negative mode	Semi-quantified
2019 Wang. [41]	Barnett shale (TX), FW; DJ basin (CO), PW	DOM	n/a	3D EEM fluorescence spectroscopy and FRI analysis	YES

2019 McAdams. [26]	Marcellus Shale (PA), FW	Alkyl ethoxylates (AEOs) and polyethylene glycols (PEGs)	SPE, SEP Pak C-18 cartridges (Waters)	LC-HRMS (Q-ToF)	NO
2018 Butkovskiy. [21]	Baltic shale (Poland), PW (after 2 months)	DOC and individual organic compounds removal during treatment	All samples filtered by 0.45 μm filter; MS sample filtered by 0.2 μm filter; Dilution.	Volatile fatty acids (VFA) and alcohols: GC-FID; Headspace gas: GC- μTCD ; Organic compounds: LC- HRMS (Linear Ion Trap Orbitrap)	Semi- quantified
2018 He. [17]	Duvernay Formation (Canada), FW	Non-target analysis and targeted PAH analysis	0.4 μm filters to separated solid and aqueous; LLE (DCM and hexane) to extract organics from liquid; SPE to clean samples, silica cartridge (Waters)	HPLC-HRMS (Orbitrap)	NO
2018 Hildenbrand. [30]	Eagle Ford (TX), PW	Comprehensive analysis of PW during treatment	No pretreatment	HSGC: VOCs; GC-MS: SVOCs.	Semi- quantified
2018 Luek. [19]	Marcellus shale (WV), fracturing fluid (FF), FW, and PW	Temporal change of halogenated organic compounds (iodinated are dominant)	Through a 0.7 mm glass fiber filter (Whatman GF/F); SPE: 1 g/6 mL Bond Elut PPL cartridges	Bruker Solarix 12T electrospray ionization FT- ICR-MS	Semi- quantified
2018 Oetjen. [6]	Niobrara formation (DJ basin, CO). FW	Temporal change of organic compounds throughout the flowback period	Hydrophobic: SPE (automated, AutoTrace 280 SPE unit), Supra-Clean C18-S cartridge (PerkinElmer); Hydrophilic: salt assisted LLE (NaCl with acetonitrile).	Hydrophilic: HPLC- MS (Q- ToF) Hydrophobic: GC-MS (Q)	Semi- quantified

2018 Oetjen. [42]	CO, HF wastewater spill simulation	5 PEGs, 8 BACs, 14 AEOs.	Filtered with 0.45 μ m PES filters; Salt assisted LLE (NaCl with acetonitrile)	LC-MS (Q-ToF)	NO
2018 Nell. [43]	Marcellus shale (WV), PW, and FW	19 HF additives, the matrix effects on the ionization efficiency	Filtered with 0.45 μ m PTFE filters; Dilution	LC-MS (Q-Orbitrap)	YES
2018 Lyman. [44]	Uinta basin (UT), Upper green river basin (WY). PW	Methane, non-methane hydrocarbons (C2-C11), light alcohols, and carbon dioxide	Purge and trap	GC-FID for light hydrocarbons (ethane, ethylene, acetylene, propane, and propylene). GC-MS for the rest compounds.	YES
2018 Riley. [25]	Piceance basin (CO) PW; Denver-Julesburg (DJ) basin (CO) PW, and DJ basin (CO) FW	Dissolved organic matter (DOC) during treatment	LC-HRMS: Salt assisted LLE (NaCl with Acetonitrile) GC-MS: automated SPE (AutoTrace 280, Thermo Scientific). Octadecyl-bonded silica cartridges	LC-MS (Q-ToF): low molecular weight organics. GC-MS (single Q): semi- volatile aliphatic and aromatic hydrocarbons. 3D fluorescence.	YES
2018 Sitterley. [28]	CO, OK, TX, WY, ND. FW and PW	Amino-poly (ethylene glycol)s, amino- poly(ethylene glycol) carboxylates, and amino- poly(ethylene glycol) amines	SPE, Oasis HLB cartridge (Waters Corporation)	HPLC-HRMS (Q-ToF)	NO
2018 Tasker. [45]	Marcellus shale (PA), FW	Organics from O&G wastewater used on a road	LLE (DCM)	GC X GC - MS (ToF): diesel and gas range organics.	NO
2018 Varona- Torres. [46]	Permian Basin, west TX. Soil	BETX in soil, close to UD activities	Room temperature ionic liquids (RTILs) as solvents for HSGC	HS-GC-MS (QQQ)	YES

2017 He. [27]	Duvernay Formation (Canada), FW	Nontarget analysis for dissolved polar organics, FW	Centrifuge and filtration, 0.22 μm PES filter. For PAHs: LLE (DCM), followed by SPE, Silica cartridges (Waters, 1g/6cc)	HPLC-HRMS (Orbitrap Elite MS): nontarget analysis. GC-MS: PAHs	PAHs were quantified
2017 Thurman. [47]	Denver-Julesburg Basin (Niobrara Formation), CO. FW and PW	Polypropylene glycols (PPG) and polyethylene glycol carboxylates (PEG-Cs) and their isomers (first time found)	Filtered through 0.2 μm PTFE filters	UHPLC- MS (Q-ToF)	Semi-quantified
2017 Luek. [18]	ND, CO, OH, WV, PA. 16 samples, FW and PW	Halogenated organic compounds	Filtered through pre-combusted 0.7 μm glass fiber filters. SPE, Agilent Bond Elut PPL SPE cartridges	Bruker Solarix 12 T FT-ICR-MS; LTQ Orbitrap XL MS for MS/MS.	NO
2016 Khan. [48]	Permian Basin (TX), PW	VOCs and SVOCs	SPME (polydimethylsiloxane (PDMS))	GC-MS (ToF)	YES
2016 Hoelzer. [49]	Fayetteville Shale (Arkansas)	Hydrocarbons, alcohols, carboxylic acids, halogenated hydrocarbons	Purge and Trap for volatile compounds; LLE for the rest (90:10 (v/v) DCM: methanol.)	GC-FID and GC-MS (Q) for volatile compounds; GC-MS, GC \times GC-MS (ToF), GC \times GC-FID for less volatile, hydrophobic substances	YES
2016 Kahrilas. [50]	Marcellus Shale (undisclosed), shale sample	Simulate transformation of Glutaraldehyde at the extreme conditions in unconventional shale reservoirs.	Derivatization with dinitrophenylhydrazine (DNPH)	HPLC-UV and HPLC-MS (ToF)	YES
2016 Regnery. [22]	DJ Basin, CO	Semi-volatile linear aliphatic hydrocarbons (n-C ₁₀ to n-C ₃₂) and 16 polycyclic aromatic hydrocarbons (PAH)	SPE, AutoTrace 280 SPE unit with Thermo Scientific Dionex SolEx C18 cartridges	GC-MS (Q)	YES

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