Supplementary Materials

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 | 5.2-470.3/ | 1.0-398.0 | 16.9-206.7 | 1.5-394.6 | 3.9-109/ | 1.2-430.4 |
|                | 15.3     | 229.2      | 199.5     | 61.3       | 162.1     | 40.3     | 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 (CaCO₃ 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-   | 12,271-    | 118,760/  | 278-28,200 | 5,311-60,106/ | 3,465-  | 1,336-   |
|                | 18,297/  | 72,299     | 278-28,200| 5,311-60,106/ | 3,465-  | 1,336-   | 316-     |
| Mg (mg/L)      | 6.3-411/ | 118-9,805/ | 1,181     | 2-757      | 34-1,772/ | 33-3,427/ | 4-170/   |
|                | 29       | 1,181      | 2-757     | 34-1,772/ | 33-3,427/ | 4-170/   | 6-18,145/ |
| Ca (mg/L)      | 20-1,501/| 18-132,687/| 13,520    | 13-6,730   | 223-17,072/ | 349-30,736/ | 19-760/   |
|                | 84       | 13,520     | 13-6,730  | 223-17,072/ | 349-30,736/ | 19-760/   | 26-46,500/ |
| Ba (mg/L)      | 0.1-39/  | 0.001-1,400/| 67       | 0.5-17.9   | 1.6-1,216/ | 0.1-22,400/ | n/a       |
|                | 5        | 67         | 0.5-17.9  | 1.6-1,216/ | 0.1-22,400/ | n/a       | 1.1-1,136/ |
| K (mg/L)       | 8.6-48/  | 30-8,526/  | 72,400    | 123,579/   | 35,926    | 80,764   | 24,093   |
|                | 28       | 4,386      | 72,400    | 123,579/   | 35,926    | 80,764   | 24,093   |
| Cl (mg/L)      | 31,667/  | 310,561/   | 142,816   | 123,579/   | 35,926    | 80,764   | 24,093   |
|                | 8,172    | 142,816    | 123,579/  | 35,926    | 80,764    | 24,093   | 95,820   |
| SO₄ (mg/L)     | 3.4-206/ | 27-6,258/  | 514       | 120-1,260  | 6.4-346/  | 0.6-199/  | 5-306/   |
|                | 94       | 514        | 120-1,260 | 6.4-346/  | 0.6-199/  | 5-306/   | 2-7,851/ |
| HCO₃ (mg/L)    | 537-1,562/| 1.9-7,355/ | 145-994   | 537-537/   | n/a       | 171-1,783/ | 7-6,346/ |
|                | 1,003    | 238        | 537       | n/a       | 619       | 440      |
| Total Ra (pCi/L)| n/a    | 786-1,722/ | n/a       | 137-558/   | 0.2-18,045/ | n/a    | 58-1,542/ |
|                |          | 1,225      | n/a       | 312       | 3,250     | 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.

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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 portioning 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. 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 | On-Site Preservation               | Holding Time               |
|----------------------------------------------|------------------------------------------|------------------|------------------------------------|----------------------------|
| **Inorganic and Wet Chemistry**              |                                          |                  |                                    |                            |
| Alkalinity                                   | SM 2320 B-1997 (Titration)               | 250 mL - Plastic | Cool to ≤ 6°C                      | 14 Days                  |
| Ammonia                                      | EPA 350.1 (Colorimetric)                 | 250 mL - Plastic | H₂SO₄ until pH < 2, Cool to ≤ 6°C  | 28 Days                   |
| Biochemical Oxygen Demand (BOD₅)             | SM 5210 B-2001 (Titrimetric)             | 1000 mL - Plastic| Cool to ≤ 6°C                      | 48 Hours                  |
| Chemical Oxygen Demand (COD)                 | EPA 410.4 (Spectrophotometric)           | 500 mL - Plastic | H₂SO₄ until pH < 2, Cool to ≤ 6°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 ≤ 6°C                      | 28 Days except NO₂, NO₃, Ortho-P 48 Hours |
| Fluoride, Chloride, Nitrite, Ortho-Phosphate, Bromide, Nitrate, Sulfate | ASTM D4327 (Suppressed Ion Chromatography) | 500 mL - Plastic | Cool to ≤ 6°C                      | 28 Days except NO₂, NO₃, Ortho-P 48 Hours |
| Hardness                                     | SM 2340B                                 | 250 mL - Plastic | HNO₃ until pH is < 2, Cool to ≤ 6°C| 6 Months                  |
| Iodide                                       | EPA 345.1                                | 250 mL - Plastic | Cool to ≤ 6°C                      | 24 Hours                  |
| Methylene Blue Active Substances (Surfactants, anionic) | EPA 425.1                                | 250 mL - Plastic | Cool to ≤ 6°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 H₂SO₄ until pH < 2, Cool to ≤ 6°C | 28 Days |

*Note: *Methods and techniques are provided for specific analytes to ensure accurate measurement and preservation. Holding times vary depending on the preservation requirements to maintain sample integrity.
| Parameter                        | Method/Standard          | Volume/mL | Container   | Treatment Notes                                      | Duration   |
|---------------------------------|--------------------------|-----------|-------------|-----------------------------------------------------|------------|
| Nitrogen, Ammonia               | SM 4500 NH3-B,C          | 500       | Plastic     | H₂SO₄ until pH < 2, Cool to ≤ 6°C                    | 28 Days    |
| Nitrogen, Total Kjeldahl        | SM 4500Norg B,C          | 500       | Plastic     | H₂SO₄ until pH < 2, Cool to ≤ 6°C                    | 28 Days    |
|                                 | SM 4500 NH3-C            |           |             |                                                     |            |
| Phenolics                       | EPA 420.4                | 1         | Glass       | H₂SO₄ until pH < 2, Cool to ≤ 6°C                    | 28 Days    |
| Phosphorous, Total              | ASTM D515                | 500       | Plastic     | H₂SO₄ until pH < 2, Cool to ≤ 6°C                    | 28 Days    |
| Salinity                        | SM 2520                  | 250       | Plastic     | Cool to ≤ 6°C                                       | 28 Days    |
| Silica                          | EPA 200.7/6010 D         | 250       | Plastic     | Cool to ≤ 6°C                                       | 28 Days    |
| Specific Conductance            | SM 2510 B-1997           | 100       | Plastic     | Cool to ≤ 6°C                                       | 28 Days    |
|                                 | (Conductivity Meter)     |           |             |                                                     |            |
| Sulfate                         | 300.0/375.4              | 500       | Plastic     | Cool to ≤ 6°C                                       | 28 Days    |
| Sulfide                         | SM 4500-S D              | 500       | Plastic     | Cool to ≤ 6°C Zn Acetate & NaOH to pH > 9          | 7 Days     |
| Sulfite                         | SM 4500 SO3-B            | 100       | Plastic     | Not required                                        | 15 Minutes |
| Total Dissolved Solids (TDS)    | SM 2540 C-1997           | 250       | Plastic     | Cool to ≤ 6°C                                       | 7 Days     |
|                                 | (Gravimetric)            |           |             |                                                     |            |
| Total Hardness                  | SM 2340 C-1997           | 250       | Plastic     | HNO₃ or H₂SO₄ until pH is < 2, Cool to ≤ 6°C        | 6 Months   |
|                                 | (Titrimetric)            |           |             |                                                     |            |
| Total Organic Carbon (TOC)      | EPA 415.1 SM 5310 B-2000 (Combustion) | 250 | Amber Glass | H₂SO₄ or H₃PO₄ until pH < 2, Cool to ≤ 6°C          | 28 Days    |
| Total Suspended Solids (TSS)    | SM 2540 D-1997           | 1000      | Plastic     | Cool to ≤ 6°C                                       | 7 Days     |
| Turbidity                       | EPA 180.1                | 100       | Plastic     | Cool to ≤ 6°C                                       | 28 Hours   |
| Metals                          |                          |           |             |                                                     |            |
| Trace elements (Total)          | EPA 200.7 (ICP), EPA 200.8/EPA 6020B (ICPMS) | 500 | Plastic | HNO₃ until pH is < 2                                 | 6 Months   |

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| Analyte                          | Methodology                          | Vial Size | Container | Preservation | Storage | Notes                        |
|---------------------------------|---------------------------------------|-----------|-----------|--------------|---------|------------------------------|
| **Trace elements**              | EPA 200.7 (ICP), EPA 200.8/EPA 6020B (ICPMS) | 500 mL    | Plastic   | 0.45 µm filtration in 15 minutes, HNO₃ until pH is < 2 | 6 Months |
|                                 | **Mercury**                           | 500 mL    | Plastic   | HNO₃ until pH is < 2 | 28 Days  |
|                                 | EPA 245.1 or 245.2 (Cold Vapor Atomic Absorption) |           |           |              |         |
| **Hexavalent Chromium**         | SM 3500 -Cr B-2009 (Colorimetric)/ EPA 7199 | 250 mL    | Plastic   | Cool to ≤ 6°C | 24 Hours |
| **Organics**                    |                                       |           |           |              |         |
| **Alcohols**                    | EPA 8260C, 8270D, and 8015C (GC/MS)   | 40-mL VOA vials | HCl until pH < 2, Cool to ≤ 6°C | 14 Days |
| **Aldehydes**                   | EPA 8315(HPLC)                        | 250 mL    | Amber Glass | Cool to ≤ 6°C | 3 Days   |
| **Diesel Range**                | EPA 3520C (sample preparation) EPA 8015C (analysis) (GC) | 1-L - Amber Glass | Cool to ≤ 6°C | 7 Days   |
| **Gasoline Range**              | EPA 5030B (sample preparation) EPA 8015C (analysis) (GC) | 40-mL VOA vials | Cool to ≤ 6°C | 7 Days   |
| **GCMS Purgeables**             | EPA 524.2                             | 40-mL VOA vials | Ascorbic acid and HCl until pH < 2, Cool to ≤ 6°C | 14 Days |
| **GCMS Purgeables**             | EPA 624/8260C                         | 40-mL VOA vials | HCl until pH < 2, Cool to ≤ 6°C | 14 Days |
| **Haloacetic Acids**            | EPA 552.2                             | 250 mL    | Amber Glass | Cool to ≤ 6°C, NH₄Cl | 14 Days |
| **Herbicides**                  | EPA 8151A (GC)                        | 1-L - Amber Glass | Cool to ≤ 6°C | 7 Days   |
| **Oil & Grease**                | EPA 1664B (Extraction and Gravimetry) | 1-L Amber Glass | HCl or H₂SO₄ until pH < 2, Cool to ≤ 6°C | 28 Days |
| **Pesticides**                  | EPA 608/8081B (GC)                    | 1-L Amber Glass | Cool to ≤ 6°C | 7 Days   |
| **Semivolatile Organic Compounds + Tentative Identified compounds** | EPA 3520C/8270D (GC/MS) | 1-L - Amber Glass | Cool to ≤ 6°C | 7 Days   |
### Semivolatile Organic Compounds + Tentative Identified compounds

- **EPA 625/8270D (GC)**
  - 1-L - Glass
  - **Cool to ≤ 6°C, Add Na₂S₂O₃ in the presence of residual chlorine**
  - **7 Days**

### Total Petroleum Hydrocarbons

- **EPA 1664B (Extraction and Gravimetry)**
  - 1-L Amber Glass
  - **HCl or H₂SO₄ until pH < 2, Cool to ≤ 6°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 ≤ 6°C**
  - **14 Days**

- **EPA 624.1 (GC/MS)**
  - 40-mL VOA vials
  - **HCl until pH < 2, Cool to ≤ 6°C, Add Na₂S₂O₃ (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
    - **HNO₃ until pH is < 2**
    - **6 Months**

- **Total Radium 228 (Liquid Samples)**
  - **EPA 904.0 (Radiochemical/Precipitation)**
    - 1-L - Plastic
    - **HNO₃ 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
    - **HNO₃ 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 ≤ 6°C**
    - **8 Hours**

- **Coliform, Fecal Strep**
  - **SM 9230A/B**
    - 250 mL - Sterile Plastic
    - **Cool to ≤ 6°C**
    - **6 Hours**

- **Coliform, Total**
  - **EPA 1603**
    - 250 mL - Sterile Plastic
    - **Cool to ≤ 6°C**
    - **8 Hours**

- **Coliform, E.Coli**
  - **EPA 1603**
    - 250 mL - Sterile Plastic
    - **Cool to ≤ 6°C**
    - **8 Hours**

- **Enterococci**
  - **EPA 1600**
    - 250 mL - Sterile Plastic
    - **Cool to ≤ 6°C**
    - **8 Hours**
Heterotrophic Plate Count

|                | SM 9215B          | 250 mL - Sterile Plastic | Cool to ≤ 6°C | 8 Hours |
|----------------|-------------------|--------------------------|---------------|---------|
| Whole Effluent Toxicity (WET) |                   |                          |               |         |
| Acute Nonvertebrate | *Ceriodaphnia dubia* | 4-L - Plastic Cubitainer | Cool to ≤ 6°C | 36 Hours |
| Acute Vertebrate   | *Pimephales promelas* | 4-L - Plastic Cubitainer | Cool to ≤ 6°C | 36 Hours |
| Chronic Nonvertebrate | *Ceriodaphnia dubia* | 4-L - Plastic Cubitainer | Cool to ≤ 6°C | 36 Hours |
| Chronic Vertebrate | *Pimephales promelas* | 4-L - Plastic Cubitainer | Cool to ≤ 6°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.

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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 ºC. 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 ºC; 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 ºC; 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. | 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        |
| [38]          |                         |                                                                                  | 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                                    |            |
| 2019 Akyon.   | Utica and Bakken shales, PW | Total, dissolved organic carbon during biological treatment                     | 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 C0-9 phenols; GC X GC-MS (ToF) and LC-HRMS (Orbitrap) for non-target analysis | YES        |
| [20]          |                         |                                                                                  |                                                                                      |                                                                                      |            |
| 2019 Sorensen.| 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. |                                                                                      | YES        |
| [24]          |                         |                                                                                  |                                                                                      |                                                                                      |            |
| 2019 Sun.     | Duvernay Formation (Canada), FPW over 30 days of flowback Bakken shale (ND), FW; Barnett shale (TX), FW; DJ basin (CO), PW | 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 |
| [40]          |                         |                                                                                  |                                                                                      |                                                                                      |            |
| 2019 Wang.    |                         | DOM                                                                             | n/a                                                                                  | 3D EEM fluorescence spectroscopy and FRI analysis                                     | YES        |
| [41]          |                         |                                                                                  |                                                                                      |                                                                                      |            |
| Year | Author                  | Location/Type | Sample | Analytical Methods |
|------|-------------------------|---------------|--------|--------------------|
| 2019 | McAdams et al. [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 | Butkovskyi et al. [21]  | Baltic shale (Poland), FW (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 et al. [17]          | Duvernay Formation (Canada), FW | Non-target analysis and targeted PAH analysis | Through a 0.7 mm glass fiber filter (Whatman GF/F); SPE: 1 g/6 mL Bond Elut PPL cartridges; Hydrophobic: SPE (automated, AutoTrace 280 SPE unit), Supra-Clean C18-S cartridge (PerkinElmer); Hydrophilic: salt assisted LLE (NaCl with acetonitrile). | HPLC-HRMS (Orbitrap) | NO |
| 2018 | Hildenbrand et al. [30] | Eagle Ford (TX), FW | Comprehensive analysis of PW during treatment | No pretreatment | HSGC: VOCs; GC-MS: SVOCs. | Semi-quantified |
| 2018 | Luek et al. [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 et al. [6]       | Niobrara formation (DJ basin, CO), FW | Temporal change of organic compounds throughout the flowback period | Through a 0.7 mm glass fiber filter (Whatman GF/F); SPE: 1 g/6 mL Bond Elut PPL cartridges; 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) | Semi-quantified |
| Year | Study | Location | Water Type | Chemicals Analyzed | Sample Preparation | Analytical Methods | Results |
|------|-------|----------|------------|-------------------|-------------------|--------------------|---------|
| 2018 Oetjen. [42] | CO, HF wastewater spill simulation | 5 PEGs, 8 BACs, 14 AEOs. | Filtered with 0.45 µm 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 µm 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), amine-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 |
| Year  | Location                          | Methodology                                                                 | Results                                                                 |
|-------|-----------------------------------|----------------------------------------------------------------------------|------------------------------------------------------------------------|
| 2017  | Duvernay Formation (Canada)        | Centrifuge and filtration, 0.22 µm PES filter. For PAHs: LLE (DCM), followed by SPE, Silica cartridges (Waters, 1g/6cc) | PAHs were quantified                                                   |
| 2017  | Denver-Julesburg Basin (Niobrara Formation, CO) | Filtered through 0.2 µm PTFE filters                                        | HPLC-HRMS (Orbitrap Elite MS): nontarget analysis. GC-MS: PAHs         |
| 2017  | ND, CO, OH, WV, PA. 16 samples, FW and PW | For PAHs: LLE (DCM), followed by SPE, Silica cartridges (Waters, 1g/6cc) | NO                                                                     |
| 2017  | Fayetteville Shale (Arkansas)      | GC-MS (ToF)                                                               | YES                                                                   |
| 2017  | Marcellus Shale (undisclosed)      | GC-MS (ToF)                                                               | YES                                                                   |
| 2016  | DJ Basin, CO                      | SPE, AutoTrace 280 SPE unit with Thermo Scientific Dionex SolEx C18 cartridges | GC-MS (Q)                                                             |

Water 2021, 13, 183. https://doi.org/10.3390/w13020183  www.mdpi.com/journal/water
References:

1. U.S.EIA. Drilling Productivity Report. 2020.
2. Fisher, C.; Jack, R. Analysis of ions in hydraulic fracturing wastewaters using ion chromatography. In Hydraulic Fracturing: Environmental Issues, ACS Publications: 2015; pp. 135-150.
3. Kim, S.; Omur-Ozbek, P.; Dhanasekar, A.; Prior, A.; Carlson, K. Temporal analysis of flowback and produced water composition from shale oil and gas operations: impact of frac fluid characteristics. Journal of Petroleum Science and Engineering 2016, 147, 202-210.
4. Rosenblum, J.; Nelson, A.W.; Ruyle, B.; Schultz, M.K.; Ryan, J.N.; Linden, K.G. Temporal characterization of flowback and produced water quality from a hydraulically fractured oil and gas well. Science of The Total Environment 2017, 596, 369-377.
5. Barbot, E.; Vidic, N.S.; Gregory, K.B.; Vidic, R.D. Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing. Environmental science & technology 2013, 47, 2562-2569.
6. Oetjen, K.; Chan, K.E.; Gulmark, K.; Christensen, J.H.; Blotevogel, J.; Borch, T.; Spear, J.R.; Cath, T.Y.; Higgins, C.P. Temporal characterization and statistical analysis of flowback and produced waters and their potential for reuse. Science of the Total Environment 2018, 619, 654-664.
7. Scanlon, B.R.; Reedy, R.C.; Xu, P.; Engle, M.; Nicot, J.; Yoxtheimer, D.; Yang, Q.; Ikonnikova, S. Can we beneficially reuse produced water from oil and gas extraction in the US? Science of The Total Environment 2020, 717, 137085.
8. Rodriguez, A.Z.; Wang, H.; Hu, L.; Zhang, Y.; Xu, P. Treatment of Produced Water in the Permian Basin for Hydraulic Fracturing: Comparison of Different Coagulation Processes and Innovative Filter Media. Water 2020, 12, 770.
9. Chang, H.; Li, T.; Liu, B.; Vidic, R.D.; Elimelech, M.; Crittenden, J.C. Potential and implemented membrane-based technologies for the treatment and reuse of flowback and produced water from shale gas and oil plays: A review. Desalination 2019, 455, 34-57.
10. Lipus, D.; Roy, D.; Khan, E.; Ross, D.; Vikram, A.; Gulliver, D.; Hammack, R.; Bibby, K. Microbial communities in Bakken region produced water. FEMS microbiology letters 2018, 365, fny107.
11. Vanderford, B.J.; Mawhinney, D.B.; Trenholm, R.A.; Zeigler-Holady, J.C.; Snyder, S.A. Assessment of sample preservation techniques for pharmaceuticals, personal care products, and steroids in surface and drinking water. Analytical and bioanalytical chemistry 2011, 399, 2227-2234.
12. Kahrilas, G.A.; Blotevogel, J.; Stewart, P.S.; Borch, T. Biocides in hydraulic fracturing fluids: a critical review of their usage, mobility, degradation, and toxicity. Environmental science & technology 2014, 49, 16-32.
13. Oetjen, K.; Giddings, C.G.; McLaughlin, M.; Nell, M.; Blotevogel, J.; Helbling, D.E.; Mueller, D.; Higgins, C.P. Emerging analytical methods for the characterization and quantification of organic contaminants in flowback and produced water. Trends in Environmental Analytical Chemistry 2017, 15, 12-23.
14. Lipus, D.; Vikram, A.; Hammack, R.; Bibby, K.; Gulliver, D. The Effects of Sample Storage Conditions on the Microbial Community Composition in Hydraulic Fracturing Produced Water. Geomicrobiology Journal 2019, 36, 630-638.
15. Santos, I.C.; Hildenbrand, Z.L.; Schug, K.A. A Review of Analytical Methods for Characterizing the Potential Environmental Impacts of Unconventional Oil and Gas Development. Analytical chemistry 2018, 91, 689-703.
16. Carlton Jr, D.D.; Hildenbrand, Z.L.; Schug, K.A. Analytical Approaches for High-Resolution Environmental Investigations of Unconventional Oil and Gas Exploration. In Advances in Chemical Pollution, Environmental Management and Protection, Elsevier: 2017; Vol. 1, pp. 193-226.
17. He, Y.; Sun, C.; Zhang, Y.; Folkerts, E.J.; Martin, J.W.; Goss, G.G. Developmental toxicity of the organic fraction from hydraulic fracturing flowback and produced waters to early life stages of Zebrafish (Danio rerio). *Environmental science & technology* **2018**, *52*, 3820-3830.

18. Luek, J.L.; Schmitt-Kopplin, P.; Mouser, P.J.; Petty, W.T.; Richardson, S.D.; Gonsior, M. Halogenated organic compounds identified in hydraulic fracturing wastewaters using ultrahigh resolution mass spectrometry. *Environmental science & technology* **2017**, *51*, 5377-5385.

19. Luek, J.L.; Harir, M.; Schmitt-Kopplin, P.; Mouser, P.J.; Gonsior, M. Temporal dynamics of halogenated organic compounds in Marcellus Shale flowback. *Water research* **2018**, *136*, 200-206.

20. Akyon, B.; McLaughlin, M.; Hernández, F.; Blotevogel, J.; Bibby, K. Characterization and biological removal of organic compounds from hydraulic fracturing produced water. *Environmental Science: Processes & Impacts* **2019**, *21*, 279-290.

21. Butkovskyi, A.; Faber, A.-H.; Wang, Y.; Grolle, K.; Hofman-Caris, R.; Bruning, H.; Van Wezel, A.P.; Rijnaarts, H.H. Removal of organic compounds from shale gas flowback water. *Water research* **2018**, *138*, 47-55.

22. Regnery, J.; Coday, B.D.; Riley, S.M.; Cath, T.Y. Solid-phase extraction followed by gas chromatography-mass spectrometry for the quantitative analysis of semi-volatile hydrocarbons in hydraulic fracturing wastewaters. *Analytical methods* **2016**, *8*, 2058-2068.

23. Cluff, M.A.; Hartsock, A.; MacRae, J.D.; Carter, K.; Mouser, P.J. Temporal changes in microbial ecology and geochemistry in produced water from hydraulically fractured Marcellus Shale gas wells. *Environmental science & technology* **2014**, *48*, 6508-6517.

24. Sørensen, L.; McCormack, P.; Altin, D.; Robson, W.J.; Booth, A.M.; Fakness, L.-G.; Rowland, S.J.; Størseth, T.R. Establishing a link between composition and toxicity of offshore produced waters using comprehensive analysis techniques–A way forward for discharge monitoring? *Science of The Total Environment* **2019**, *694*, 133682.

25. Riley, S.M.; Ahoor, D.C.; Regnery, J.; Cath, T.Y. Tracking oil and gas wastewater-derived organic matter in a hybrid biofilter membrane treatment system: A multi-analytical approach. *Science of the Total Environment* **2018**, *613*, 208-217.

26. McAdams, B.C.; Carter, K.E.; Blotevogel, J.; Borch, T.; Hakala, J.A. In situ transformation of hydraulic fracturing surfactants from well injection to produced water. *Environmental Science: Processes & Impacts* **2019**, *21*, 1777-1786.

27. He, Y.; Flynn, S.L.; Folkerts, E.J.; Zhang, Y.; Ruan, D.; Alessi, D.S.; Martin, J.W.; Goss, G.G. Chemical and toxicological characterizations of hydraulic fracturing flowback and produced water. *Water research* **2017**, *114*, 78-87.

28. Sitterley, K.A.; Linden, K.G.; Ferrer, I.; Thurman, E.M. Identification of proprietary amino ethoxylates in hydraulic fracturing wastewater using liquid chromatography/time-of-flight mass spectrometry with solid-phase extraction. *Analytical chemistry* **2018**, *90*, 10927-10934.

29. Hickenbottom, K.L.; Hancock, N.T.; Hutchings, N.R.; Appleton, E.W.; Beaudry, E.G.; Xu, P.; Cath, T.Y. Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. *Desalination* **2013**, *312*, 60-66.

30. Hildenbrand, Z.L.; Santos, I.C.; Liden, T.; Carlton Jr, D.D.; Varona-Torres, E.; Martin, M.S.; Reyes, M.L.; Mulla, S.R.; Schug, K.A. Characterizing variable biogeochemical changes during the treatment of produced oilfield waste. *Science of the Total Environment* **2018**, *634*, 1519-1529.

31. Wasylischen, R.; Fulton, S. Reuse of flowback and produced water for hydraulic fracturing in tight oil. *Pet. Technol. Alliance Can* 2012.

32. U.S.EPA. Clean Water Act Analytical Methods. 2019.

33. U.S.EPA. EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes. 1983.

34. Mass (1990) Crop salt tolerance. In: Agricultral Assessment and Mangament Manual.
35. Rice, E.W.; Baird, R.B.; Eaton, A.D.; Clesceri, L.S. Standard methods for the examination of water and wastewater. *American Public Health Association, Washington, DC* 2012, 541.

36. EPA, U. Method 415.3: Determination of Total Organic Carbon and Specific UV Absorbance at 254 Nm in Source Water and Drinking Water. Revision: 2009.

37. Potter, B.; Wimsatt, J. Method 415.3. Measurement of total organic carbon, dissolved organic carbon and specific UV absorbance at 254 nm in source water and drinking water. *US Environmental Protection Agency, Washington, DC* 2005.

38. Almaraz, N.; Regnery, J.; Vanzin, G.F.; Riley, S.M.; Ahoor, D.C.; Cath, T.Y. Emergence and fate of volatile iodinated organic compounds during biological treatment of oil and gas produced water. *Science of the Total Environment* 2020, 699, 134202.

39. International, A. Standard Test Method for Total Nitrogen, and Total Kjeldahl Nitrogen (TKN) by Calculation, in Water by High Temperature Catalytic Combustion and Chemiluminescence Detection. 2016.

40. Sun, C.; Zhang, Y.; Alessi, D.S.; Martin, J.W. Nontarget profiling of organic compounds in a temporal series of hydraulic fracturing flowback and produced waters. *Environment international* 2019, 131, 104944.

41. Wang, H.; Lu, L.; Chen, X.; Bian, Y.; Ren, Z.J. Geochemical and microbial characterizations of flowback and produced water in three shale oil and gas plays in the central and western United States. *Water research* 2019, 164, 114942.

42. Oetjen, K.; Blotevogel, J.; Borch, T.; Ranville, J.F.; Higgins, C.P. Simulation of a hydraulic fracturing wastewater surface spill on agricultural soil. *Science of the Total Environment* 2018, 645, 229-234.

43. Lyman, S.N.; Mansfield, M.L.; Tran, H.N.; Evans, J.D.; Jones, C.; O’Neil, T.; Bowers, R.; Smith, A.; Keslar, C. Emissions of organic compounds from produced water ponds I: Characteristics and speciation. *Science of the Total Environment* 2018, 619, 896-905.

44. Tasker, T.; Burgos, W.D.; Piotrowski, P.; Castillo-Meza, L.; Blewett, T.; Ganow, K.; Stallworth, A.; Delompré, P.; Goss, G.; Fowler, L.B. Environmental and human health impacts of spreading oil and gas wastewater on roads. *Environmental science & technology* 2018, 52, 7081-7091.

45. Varona-Torres, E.; Carlton Jr, D.D.; Hildenbrand, Z.L.; Schug, K.A. Matrix-effect-free determination of BTEX in variable soil compositions using room temperature ionic liquid co-solvents in static headspace gas chromatography mass spectrometry. *Analytica chimica acta* 2018, 1021, 41-50.

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

47. Khan, N.A.; Engle, M.; Dungan, B.; Holguin, F.O.; Xu, P.; Carroll, K.C. Volatile-organic molecular characterization of shale-oil produced water from the Permian Basin. *Chemosphere* 2016, 148, 126-136.

48. Hoelzer, K.; Sumner, A.J.; Karatum, O.; Nelson, R.K.; Drollette, B.D.; O’Connor, M.P.; D’Ambro, E.L.; Getzinger, G.J.; Ferguson, P.L.; Reddy, C.M. Indications of transformation products from hydraulic fracturing additives in shale-gas wastewater. *Environmental science & technology* 2016, 50, 8036-8048.

49. Kahrilas, G.A.; Blotevogel, J.; Corrin, E.R.; Borch, T. Downhole transformation of the hydraulic fracturing fluid biocide glutaraldehyde: implications for flowback and produced water quality. *Environmental science & technology* 2016, 50, 11414-11423.