

**THE STATE OF NEW MEXICO
DEPARTMENT OF ENERGY, MINERALS AND NATURAL RESOURCES
OIL CONSERVATION COMMISSION**

IN THE MATTER OF PROPOSED
AMENDMENT TO THE COMMISSION'S
RULES TO ADDRESS CHEMICAL DISCLOSURE AND
THE USE OF PERFLUOROALKYL AND
POLYFLUOROALKYL SUBSTANCES AND
IN OIL AND GAS EXTRACTION,
19.15.2, 19.15.7, 19.15.14, 19.15.16 AND 19.15.25 NMAC.

Petitioner.

CASE NO. 23580

**NEW ENERGY ECONOMY'S NOTICE OF INTENT
TO PRESENT REBUTTAL TECHNICAL TESTIMONY AND EXHIBIT OF
KRISTEN HANSEN, Ph.D.**

This Notice of Intent to Present Rebuttal Technical Testimony and Exhibit of Kristen Hansen Ph.D. is submitted on behalf of New Energy Economy ("NEE") through its undersigned counsel, as required by Rule 19.15.3.11 NMAC and the Amended Procedural Order filed in this matter on June 3, 2024.

On behalf of thousands of New Mexicans, New Energy Economy hereby gives notice of its intent to present technical testimony at the hearing in this matter scheduled to begin on November 12, 2024 before the New Mexico Oil Conservation Commission ("OCC").

(1) New Energy Economy intends to present the rebuttal technical testimony of the following technical witness:

KRISTEN HANSEN, Ph.D., Savanna Science Consulting.

(2) Ms. Hansen supports the Amended Application for Rulemaking, filed on August 23, 2024 by WildEarth Guardians, entitled "In the Matter of proposed Amendment to the Commission's Rules to Address Chemical Disclosure and the Use of Perfluoroalkyl and

Polyfluoroalkyl Substances and in Oil and Gas Extraction, 19.15.2, 19.15.7, 19.15.14, 19.15.16 AND 19.15.25 NMAC.”

(3) Ms. Hansen’s qualifications including a description of the witness’ education and experience were submitted on October 21, 2024 with New Energy Economy’s Notice of Intent to Present the Direct Technical Testimony of Kristen Hansen Ph.D., which also included her Direct Testimony and Exhibits, including KH-1, her Curriculum Vitae and Publications.

(4) Attached hereto as NEE Exhibit B, please see the Rebuttal Testimony and of Kristen Hansen, Ph.D. of Savanna Science Consulting.

(5) New Energy Economy anticipates that it will offer the following exhibits at the hearing in this matter:

a. NEE Exhibit A: Direct Technical Testimony and Exhibits of Kristen Hansen, Ph.D. of Savanna Science Consulting, including:

- i. **Exhibit KH-1** – Curriculum Vitae and Publications for Kristen Hansen, Ph.D.
- ii. **Exhibit KH-2** – Lerner, Sharon. “How 3M Discovered, Then Concealed, the Dangers of Forever Chemicals,” *New Yorker*, May 20, 2024.
- iii. **Exhibit KH-3** – “Opinion: We agree PFAS should not be used in fracking, and it is not” by Lynn Granger & Dan Haley, *The Denver Post*, March 22, 2022.

b. NEE Exhibit B: Rebuttal Technical Testimony and Exhibit of Kristen Hansen, Ph.D. of Savanna Science Consulting, including:

- i. **Exhibit KH-4** – Jiang, Wenbin, et al., (2022) “Characterization of produced water and surrounding surface water in the Permian Basin, the United States,” [Journal of Hazardous Materials](#) 430: 128409.

c. New Energy Economy reserves the right to use other exhibits during cross-examination at hearing.

(6) New Energy Economy expects that the summary of the direct and rebuttal testimony of this technical witness will require the twenty minutes permitted by 19.15.3.11 B(2) NMAC and Numbered Paragraph 3 of the Amended Procedural Order of June 2, 2024.

(7) New Energy Economy requests an opportunity to provide an opening statement (20 minutes) and closing statement (30 minutes), (perhaps re-direct and surrebuttal), and sufficient time to cross-examine witnesses at the hearing (to be determined once the direct and rebuttal pre-filed witnesses' testimonies are reviewed).

(8) Regarding Scheduling: Counsel for New Energy Economy, Mariel Nanasi, has had plans to be out of the country and requests to be excused on November 12 and 13, 2024 with the understanding that New Energy Economy waives objection for the time of her absence. Further, Ms. Hansen has a scheduling conflict on the morning of Thursday November 14 and requests to testify in the afternoon of Thursday November 14th. Ms. Hansen is available to testify at 1pm Mountain Time on November 14, 2024 via the electronic platform.

Respectfully submitted this 4th day of November 2024,

NEW ENERGY ECONOMY



Mariel Nanasi, Esq.

300 East Marcy St.

Santa Fe, NM 87501

(505) 469-4060

mariel@seedsbeneaththesnow.com

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CASE NO. 23580

REBUTTAL TECHNICAL TESTIMONY AND EXHIBIT

OF

KRISTEN HANSEN, Ph.D.
Savanna Science Consulting

ON BEHALF OF
NEW ENERGY ECONOMY

November 4, 2024

1 **Q. Did you provide Direct Technical Testimony on October 21, 2024?**

2 A. Yes, on behalf of New Energy Economy (“NEE”).

3 **Q. Do you understand that WildEarth Guardians’ proposed definition of PFAS**

4 **Chemicals is as follows: “PFAS chemicals” means a perfluoroalkyl or polyfluoroalkyl**

5 **substance with at least one fully fluorinated carbon atom. What is your expert testimony**

6 **regarding that definition?**

7 A. Yes, I read WildEarth Guardian’s (WEG) definition in their proposed Amendments to

8 19.15.2.7 NMAC. WEG’s proposed definition of PFAS is consistent with my definition; it is

9 the layperson’s equivalent of my more chemically accurate definition. Further, I understand

10 that the definition suggested by WEG is the definition that has been adopted in statute in 23

11 states. I agree that this definition is adequate to ensure accurate understanding and

12 monitoring of PFAS risk.

13 **Q. Did you read the Self-Affirmed Statement of NMOGA witness Stephen D.**

14 **Richardson filed on October 21, 2024?**

15 A. Yes.

16 **Q. Did you agree with Mr. Richardson, Self-Affirmed Statement at 11, that “using the**

17 **definition WEG proposes makes no practical or technical sense in the context of this**

18 **rulemaking” because “these single -CF3 and -CF2- compounds are not known to be**

19 **utilized in hydraulic fracturing operations for oil and gas”?**

20 A. No. I don’t agree with Mr. Richardson’s opinion. The production and utilization of PFAS

21 compounds such as fluoropolymers and fluorosurfactants include a significant percentage of

1 both PFAS impurities and PFAS residuals. Whether or not a PFAS compound is specifically
2 produced for use by the industry, residual PFAS of a different structure may be present in the
3 overall formulation. It is the responsibility of the industry to control the use of both the
4 compounds produced for their purposes and additional PFAS compounds that are part of that
5 final formulation, including residuals and impurities. Additionally, many PFAS as well as
6 the impurities and residuals present in a PFAS product may undergo some level of
7 degradation in the environment resulting in a smaller, persistent perfluorinated compound.
8 Again, the industry needs to control not only the chemicals necessary for their processes but
9 also the eventual breakdown products of those PFAS into shorter chain long-lived molecules.
10 These residuals, impurities and degradation products are covered by the broader definition I
11 have proposed.

12 **Q. Did you read the Self-Affirmed Statement of NMOGA witness Janet Anderson filed**
13 **on October 21, 2024?**

14 A. Yes.

15 **Q. Ms. Anderson at p. 11 of her statement states: “Thus, revising the definition of**
16 **“PFAS” to be “substances with two or more sequential fully fluorinated carbons” is**
17 **both consistent with existing federal regulations defining the PFAS and is supported by**
18 **the science on PFAS. Furthermore, defining PFAS in this manner addresses those**
19 **chemicals potentially relevant to oil and gas operations and includes the PFAS with**
20 **data available to assess potential human and/or environmental impacts (i.e., human and**
21 **ecological toxicity data for risk assessments).” What is your response?**

1 A. As above, this definition is too narrow to be protective of humans and the environment.
2 The specific PFAS used by the O&G industry are not pure compounds, but are available with
3 measurable levels of residuals, impurities and breakdown products. It is environmentally
4 and chemically simplistic to say that adequate control is achieved using a definition only
5 relevant to a particular industry. PFAS are exceptionally stable in the environment; most are
6 highly mobile; recent research suggests that toxicity of PFAS compounds is additive. These
7 characteristics of the class indicate a need for a broad, inclusive definition to describe
8 existing and potential risk.

9 Further, at least 23 states have adopted a scientifically grounded definition of PFAS as
10 organic chemicals containing “at least one fully fluorinated carbon atom” including: AR,
11 AZ, CA, CO, CT, GA, KY, HI, IL, IN, LA, MD, ME, MN, NH, NV, NY, OH, OR, RI, VA,
12 VT, and WA. (Additional U.S. States Ban PFAS-Containing Products. (n.d.). UL Solutions.
13 Retrieved October 31, 2023. [https://www.ul.com/news/additional-us-states-ban-pfas-](https://www.ul.com/news/additional-us-states-ban-pfas-containing-products)
14 [containing-products](https://www.ul.com/news/additional-us-states-ban-pfas-containing-products)) Similarly, Congress has often adopted the same definition of PFAS, for
15 example in enacting the National Defense Authorization Act in 2021, 2022 and 2023. (See,
16 for example, the NDAA for FY2022, Public Law 117-81 (passed the Senate by a vote of 88-
17 11 & House by 363-70), §345(f)(4)(“The term ‘perfluoroalkyl or polyfluoroalkyl substance’
18 means any man-made chemical with at least one fully fluorinated carbon atom.”); The
19 NDAA for FY2021, Public Law 116-283 (passed the Senate by a vote of 81-13 & House by
20 322-87) § 335(e)(2)(“The term ‘PFAS’ means a perfluoroalkyl or polyfluoroalkyl substance
21 with at least one fully fluorinated carbon atom, including the chemical GenX.”); The NDAA
22 for FY2020, Public Law 116-92 (passed the Senate by a vote of 86-8 and House by 377-48) §
23 332(c)(3)(“The term “PFAS” means perfluoroalkyl and polyfluoroalkyl substances that are

1 man-made chemicals with at least one fully fluorinated carbon atom.”). This definition has
2 been used in state and federal legislation since 2018. (State of Washington Department of
3 Ecology. (2021). Interim Chemical Action Plan for Per- and Polyfluorinated Alkyl
4 Substances. <https://apps.ecology.wa.gov/publications/documents/1804005.pdf>, at 1.)

5 **Q. Ms. Anderson at p. 7 of her statement states: 7. “For this reason, the term “PFAS”**
6 **should be more specifically enumerated and must delineate between PFAS for which**
7 **there is toxicology data and potential concerns for human health risks and those PFAS**
8 **for which no such data or concerns exist. Statements regarding potential human or**
9 **environmental risk must be limited to the compounds for which data are available to**
10 **inform what exposure levels may present an unacceptable increase in risk, on a**
11 **chemical-specific nature.” What is your response?**

12 A. This view represents a backward-looking assessment of risk, something particularly
13 dangerous for compounds that are persistent and that, as a class, have so often been
14 demonstrated to bioaccumulate and exhibit chronic toxic effects. Current research indicates
15 that the toxicity associated with PFAS is additive, that is, that PFAS toxicity needs to be
16 understood as exposure to all PFAS present in a person’s environment, rather than as
17 exposure to a single compound (Addicks, Rowan-Carroll et al. 2023). Chronic toxicity in
18 humans is difficult and expensive to study and, with the possible exception of PFOS and
19 PFOA, many toxicologists argue that existing data on the over 10,000 members of the PFAS
20 class is incomplete (Cousins, DeWitt et al. 2020). Many PFAS compounds pass through the
21 placental barrier when they have the potential to impact gestational health (Blake and Fenton
22 2020). Many PFAS pass from mother to infant via breastfeeding (Zheng, Schreder et al.
23 2021). These are two examples of routes of exposure that have been toxicologically

1 characterized for the first time in the last 10 years despite the fact that the most well-
2 characterized PFAS, PFOS and PFOA, have been present in commercial products since the
3 early 1970s.

4 **Q. Ms. Anderson at p. 3 of her statement states: “And some PFAS do not have an**
5 **association with a wide range of potential human or ecological health effects, although**
6 **robust toxicological information on the majority of PFAS is lacking.” What is your**
7 **response?**

8 A. The uncontrolled nature of the production, utilization and environmental disposition –
9 coupled with the persistence, bioaccumulation potential, mobility and potential toxicity -
10 associated with PFAS, make members of the class suitable for application of the
11 precautionary principle. The precautionary principle states that, especially in the case of
12 persistent compounds with potential toxicological implications, decision makers err on the
13 side of caution. That is, any scientific uncertainty must be resolved by prevention. With
14 over 10,000 PFAS, it is currently impossible to fully study the toxicological effects of each
15 of these compounds alone and in combination with other PFAS. Therefore, decision makers
16 faced with decision of irreversible or slowly reversible potential human health and
17 environmental consequences should avoid risk (Cousins, Vestergren et al. 2016).

18 **Q. Ms. Anderson at p. 4 of her statement states: “Some compounds broadly identified**
19 **as PFAS (i.e., compounds that contain a single fully fluorinated methyl or methylene**
20 **carbon moiety) are routinely used as pharmaceuticals, prescribed to children and**
21 **adults[.]” If it’s true that some of the PFAS that fall under the single fluorinated carbon**
22 **atom definition are not toxic or are not toxic in low doses, isn’t the inverse true?**

1 A. Pharmaceuticals and drug products (e.g. metered dose inhalers) are subject to a much
2 more rigorous review and much tighter specifications than other areas of commerce.
3 Toxicity studies associated with pharmaceuticals are carried out in thousands of people in
4 well-controlled and well-documented studies with exposure strictly characterized and
5 controlled and health effects measured. Often side effects are noted in these studies and
6 these must be weighed against the potential therapeutic effects before the compounds are
7 approved. The pharmaceutical products themselves must meet exceptionally high
8 specifications for residuals and impurities several steps back into the supply chain, so
9 production is absolutely controlled and so that levels of impurities and residuals meet tight,
10 science-based specifications. This level of control and purity is not required in other
11 industries. It is misleading to state that a pharmaceutical compound, every lot of which is
12 characterized to meet high qualification specifications, administered in a controlled dose
13 under the care of a physician targeting a specific physiological endpoint is similar to an
14 uncontrolled environmental exposure that a community member may unknowingly encounter
15 by breathing polluted air or drinking contaminated water, for example. Further, it is
16 increasingly apparent that the toxicity associated with PFAS exposure needs to be considered
17 as an additive rather than a singular exposure, thus any certainty about exposure to one PFAS
18 must be evaluated in concert with other potential PFAS in that or other environmental
19 exposures.

20 **Q. Did you read OCD Exhibit 1 and the proposed definition of PFAS: “PFAS**
21 **chemicals” means any chemical with at least a perfluorinated methyl group (–CF₃) or a**
22 **perfluorinated methylene group (–CF₂–), excluding those with a Hydrogen [H],**
23 **Chlorine [Cl], Bromine [Br], or Iodine [I] atom attached to the subject carbon atom.**

1 **For the purposes of completing environmental investigations, the specific PFAS**
2 **chemicals that can be included in the chemical analysis include those listed in United**
3 **States Environmental Protection Agency (US EPA) Standard Analytical Methods**
4 **documents (specifically, Method 537.1 [drinking water], Method 533 [drinking water],**
5 **Method 8327 [groundwater, surface water, and wastewater], Method 1633 [wastewater,**
6 **surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue],**
7 **OTM-45 [air: semi-volatile and particulate-bound PFAS], and OTM-50 [air: volatile**
8 **PFAS]; including updated versions for each standard method).**

9 A. Yes, I read it.

10 **Q. What is your expert opinion of the use of OCD's definition?**

11 A. The OCD definition is inadequate; it is too narrow and leaves many PFAS compounds
12 unregulated. I believe that the Commission should either adopt the WEG definition or my
13 definition of PFAS, as both encompass the full class of PFAS. The first sentence of OCD's
14 definition matches that proposed in 2021 by the Organization for Economic Cooperation and
15 Development (OECD 2021). However, subsequent sentences serve only to artificially limit
16 the definition of PFAS to those compounds that have been characterized and for which
17 purified standards are available. This named subset of PFAS represents less than 5% of the
18 total number of PFAS compounds characterized as present in industrial, environmental and
19 metabolic studies and is often referred to as the "tip of the PFAS Iceberg." The methods cited
20 measure only a relatively small number of "Targeted PFAS" compounds while a much larger
21 population of "Non-targeted" PFAS remain undisclosed and uncharacterized (Manz 2024).
22 Recent advances in analytical techniques such as high-resolution mass spectrometry have

1 enabled the identification of many previously unknown or uncharacterized PFAS compounds
2 in environmental samples. For example, a 2023 study characterizing suspended particulates
3 in surface water found a 25% gap between the compound specific targeted analysis and the
4 larger extractable organic fluorine fraction of PFAS compounds (Simon, Gehrenkemper et al.
5 2023). Another study of tap water found that less than half of the organic fluorine was
6 characterized by these targeted methods (Hu, Tokranov et al. 2019). In environmental
7 samples, this gap is expected to be much larger (Dixit, Antell et al. 2024). Currently, the EPA
8 is evaluating the utility of non-targeted analysis for characterization of the full suite of PFAS
9 compounds present in drinking water (for example) to better characterize human health risk
10 (Manz, Feerick et al. 2023). The human health implications associated with these additional
11 PFAS compounds are unknown and unstudied (Steeves, Cahill et al. 2024), though recent
12 work suggests that toxicity associated with PFAS compounds may be additive (Conley,
13 Lambright et al. 2023).

14 Given the high level of environmental mobility, the incompleteness of existing toxicity and
15 human health data and the environmental durability of PFAS compounds, to ensure
16 protection of human and environmental health, the only acceptable definition of PFAS is a
17 class of compounds including chemicals with at least one aliphatic perfluorocarbon moiety (-
18 C_n-F_{2n}-). I am also supportive of the definition offered by WEG.

19 **Q. Do you believe that lack of familiarity with the specifics of the O&G industry should**
20 **bar your testimony?**

21 A. No. I have a PhD in analytical chemistry that I have used extensively to track and
22 measure anthropogenic compounds in the environment including in the atmosphere and in

1 water ways. Specifically, I have conducted pioneering work measuring and tracking PFAS
2 compounds in a variety of matrices including in water, sediment, sludge, industrial waste,
3 soil, WWTP influent and effluent, tissue, food and product samples. My work tracking PFAS
4 compounds in the environment has been cited thousands of times in the peer-reviewed
5 scientific literature. My PFAS expertise is especially germane given that these compounds
6 are both highly persistent and highly mobile in the environment, typically moving quickly
7 and widely from their point of use, discharge or disposal. With the potential for PFAS spills
8 on the ground or in water ways, volatilization of incompletely combusted PFAS during flare
9 off, volatilization of PFAS from surface ponds, spills or discharge of produced water and the
10 presence of PFAS on and from surfaces and machinery encountered during transport, use and
11 disposal, my experience with environmental analysis is far more relevant than industry-
12 specific knowledge. Any one of these PFAS exposure routes could lead to wider
13 environmental or human exposure to persistent, mobile and potentially toxic chemicals.
14 Detailed industry knowledge is not needed to identify areas of risk in the use of PFAS in the
15 environment.

16 **Q. Did you read Ms. Troutman's testimony?**

17 A. Yes, I did.

18 **Q. What was striking about the information contained therein?**

19 A. Between 2010 and 2024, the numbers of self-reported spills by the O&G industry
20 indicate over 10,000 instances of produced water spills totaling over a million gallons of
21 produced water spilled. Of those spills, 187 reached a water course and 99 spills affected

1 groundwater. Given that PFAS has been demonstrated to be present in produced water
2 (Jiang, 2022) and the persistence of PFAS compounds in the environment, it is likely that
3 essentially all the PFAS ever spilled in surface or groundwater during this 14-year reporting
4 period is still present and mobile in the environment or present in a living being, either in its
5 original form or as a terminal PFAS degradation product. I include the Jiang study as Exhibit
6 KH-4.

7 **Q. Does this conclude your rebuttal testimony?**

8 A. Yes, it does.

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6 Concerning Trends for Current-Use PFAS." Environmental Science & Technology **55**(11):
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8
9 **Exhibit Attached:**

10 KH-4: Jiang, et al., (2022) "Characterization of produced water and surrounding surface
11 water in the Permian Basin, the United States," Journal of Hazardous Materials 430: 128409.

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CASE NO. 23580

SELF AFFIRMATION

Kristen Hansen, expert witness for New Energy Economy, upon penalty of perjury under the laws of the state of Minnesota, affirm and state: I have read the foregoing Rebuttal Technical Testimony and Exhibit of Kristen Hansen and it is true and correct based on my own personal knowledge and belief.

Dated this 4th day of November 2024.

/s/ Kristen Hansen
KRISTEN HANSEN



Contents lists available at ScienceDirect

Journal of Hazardous Materials

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Research Paper

Characterization of produced water and surrounding surface water in the Permian Basin, the United States

Wenbin Jiang^a, Xuesong Xu^a, Ryan Hall^b, Yanyan Zhang^a, Kenneth C. Carroll^c, Frank Ramos^d, Mark A. Engle^e, Lu Lin^a, Huiyao Wang^a, Matthias Sayer^b, Pei Xu^{a,*}

^a Department of Civil Engineering, New Mexico State University, Las Cruces^b NGL Partners LP, Santa Fe, NM 87501, United States^c Department of Plant and Environmental Science, New Mexico State University, Las Cruces^d Department of Geological Sciences, New Mexico State University, Las Cruces^e Department of Earth, Environmental and Resource Sciences, The University of Texas at El Paso, El Paso, Texas, United States

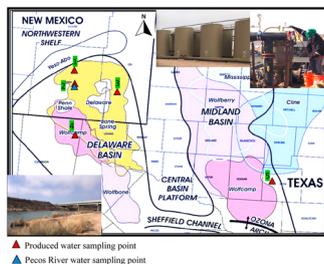
United States



HIGHLIGHTS

- Comprehensive analyses of produced water (PW) quality in the Permian Basin.
- Temporal characterization of PW and river water quality in the Permian Basin.
- Quantitatively analyzed > 300 analytes for organics, inorganics, and radionuclides.
- Provide baseline analytical information to advance PW research for potential reuse.
- Filled knowledge gap regarding PW quality to support science-based decision making.

GRAPH



ARTICLE INFO

Editor: Dr. B. Lee

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Produced water characterization
Permian Basin
Pecos river
Water reuse

ABSTRACT

A thorough understanding of produced water (PW) quality is critical to advance the knowledge and tools for effective PW management, treatment, risk assessment, and feasibility for beneficial reuse outside the oil and gas industry. This study provides the first step to better understand PW quality to develop beneficial reuse programs that are protective of human health and the environment. In total, 46 PW samples from unconventional operations in the Permian Basin and ten surface water samples from the Pecos River in New Mexico were collected for quantitative target analyses of more than 300 constituents. Water quality analyses of Pecos River samples could provide context and baseline information for the potential discharge and reuse of treated PW in this area. Temporal PW and river water quality changes were monitored for eight months in 2020. PW samples had total dissolved solids (TDS) concentrations ranging from 100,800–201,500 mg/L. Various mineral salts, metals, oil and grease, volatile and semi-volatile organic compounds, radionuclides, ammonia, hydraulic fracturing additives, and per- and polyfluoroalkyl substances were detected at different concentrations. Chemical characterization of organic compounds found in Pecos River water showed no evidence of PW origin. Isometric log-ratio Na-Cl-Br analysis showed the salinity in the Pecos River samples appeared to be linked to an increase in natural shallow brine inputs. This study outlines baseline analytical information to advance PW research by describing PW and surrounding surface water quality in the Permian Basin that will assist in determining management

* Corresponding author.

E-mail addresses: pxu@nmsu.edu, wxpei@hotmail.com (P. Xu).<https://doi.org/10.1016/j.jhazmat.2022.128409>

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strategies, treatment methods, potential beneficial reuse applications, and potential environmental impacts specific to intended beneficial use of treated PW.

1. Introduction

The rapid development of the unconventional oil and gas (O&G) industry has promoted economic growth and generated large volumes of produced water (PW) in the southwestern United States (U.S.EIA, 2021). PW is primarily naturally occurring water that emerges from the ground during the production of oil or gas (also known as formation water). Additionally, PW may include water injected into the formation during well treatment or enhanced O&G recovery (EOR), as well as flowback water that returns to the surface after hydraulic fracturing (HF) (GWPC, 2019; Scanlon et al., 2017). An estimated $3180 \times 10^6 \text{ m}^3$ (20 billion barrels) of PW will be generated by onshore O&G activities in the United States in 2022 (IHS Markit, 2020). Such large volumes of PW require appropriate management to reduce disposal costs and environmental impacts. Currently, major PW management methods include saltwater disposal (SWD) well injection, reinjection for EOR, and reuse for HF; only a very small percentage of PW (1.3% in 2017) is used outside the O&G field for irrigation and dust control on roads (Jiang et al., 2021b; U.S.EPA, 2020; Veil, 2020).

Following appropriate treatment, treated PW could prove to be an alternative water supply for other industrial applications as well thus serving to reduce stress on local water supplies. PW recycling for HF has been implemented as an economically attractive and environmentally friendly method by the O&G industry (Scanlon et al., 2020a). One challenge for PW recycling is temporally and geographically matching water demand for HF with PW supply (Jiang et al., 2021b), and that PW volume may exceed HF water demand in some areas, such as in the Permian Basin (Scanlon et al., 2020a). PW could also be treated and beneficially reused outside the O&G field to alleviate local water stress. For example, the Permian Basin is in a semi-arid region where treated PW can be used as an alternative water source to replace and augment freshwater supplies. Scanlon et al. estimated that PW, if treated and used, could represent < 1%, 5%, and 11% of irrigation water demand in Eddy, Lea, and Pecos counties, respectively, (the highest irrigation counties in the Permian Delaware Basin) after meeting the HF water demand (Scanlon et al., 2020b).

Use of treated PW for agriculture or wildlife is currently allowed west of the 98th meridian under the Oil and Gas Extraction Effluent Guidelines and Standards (40 CFR Part 435 Subpart E) in the United States. PW reuse outside the O&G field for agriculture and wildlife propagation primarily occurs in California and Wyoming because some PW in these regions has lower total dissolved solids (TDS) and may only need moderate treatment (Navarro et al., 2016; U.S.EPA, 2020). Constituents in PW vary with geographic location, reservoir lithology, geologic history, the type of hydrocarbon product being produced, and well age, which makes it difficult to fully characterize PW composition, including adequately understanding spatial and temporal variability in the production (volumes) and composition (Oetjen et al., 2018; Wang et al., 2019). Typically, PW is highly saline and could contain many different constituents such as suspended particles, dissolved mineral salts, organic compounds (e.g., volatile and semi-volatile organics (VOCs and SVOCs), petroleum hydrocarbons, organic acids, and oils), naturally-occurring radioactive material (NORM), other inorganic constituents (e.g., sulfide and ammonia), chemical additives and their transformational byproducts during well treatment or from the interactions with formation water (Jiang et al., 2021a; Rodriguez et al., 2020). Extensive treatment is required to remove these constituents for safe reuse of treated PW, which can include settling, media filtration, coagulation, chemical precipitation, adsorption, biological treatment, membrane desalination, thermal distillation, and advanced oxidation processes (Chen et al., 2021, 2022; Geza et al., 2018; Hickenbottom et al., 2013;

Hu et al., 2020; Lin et al., 2020; Ma et al., 2018; Xu and Drewes, 2006; Xu et al., 2008a, 2008b).

One of the barriers to use treated PW as an alternative water source is the lack of comprehensive chemical characterization of PW quality (Scanlon et al., 2020b). To date, most studies devoted to PW characterization are focused on the Appalachian Basin (Danforth et al., 2020). Some previous research on the Niobrara (Oetjen et al., 2018), the Barnett (Wang et al., 2019), the Bakken (Shrestha et al., 2018), and the Eagle Ford (Hildenbrand et al., 2018) also exists. The Permian Basin in southeastern New Mexico and western Texas (Fig. 1(a)) is the most productive oil province in the U.S., which accounted for almost 60% of onshore oil production in July 2021 (U.S.EIA, 2021). However, there are limited studies focused on the characterization of PW in the Permian Basin, especially the PW from unconventional wells. Most PW samples from the Permian Basin in the United States Geological Survey (USGS) database (approximately 3800 datasets for the Permian out of 114,993 total datasets in the 'USGSPWDBv 2.3 n.csv' file) were collected before 2002, and primarily from conventional wells. Only 39 samples (out of 3800 datasets) are from 2016 with limited inorganic information (Chaudhary et al., 2019; Engle et al., 2016; USGS, 2021). Our previous research identified VOCs in eight unconventional PW samples; however, it was limited in scope to the Midland Basin (the eastern portion of the Permian Basin, Texas) and did not fully characterize PW samples to a level sufficient to support hazard and risk assessment. The same limited scope of analysis and sampling is reflected in the broader literature (Hu et al., 2020; Rodriguez et al., 2020; Thacker et al., 2015). Thus, comprehensive chemical characterization and risk assessment of PW is necessary for potential treatment and beneficial use outside the O&G field in the Permian Basin.

In this study, we conducted a target analysis of physical and chemical water quality characteristics on PW samples from five locations in the Permian Basin and water samples from one location on the Pecos River (the river flowing through the Permian Basin) location in Carlsbad, New Mexico (Fig. 1(a)). Twenty-four PW samples were collected from the Permian Basin in New Mexico and Texas - 14 samples (PW-NM) from Sampling Point 2 and 10 samples (PW-TX) from Sampling Point 5 as shown in Fig. 1(a). Samples were analyzed for wet chemistry, inorganics, organics, microbial community, and toxicity. This paper reports results of physicochemical analyses, while microbial community and toxicity analyses are reported in a separate paper (Hu et al., 2022). Among these 24 samples, ten samples were collected from an SWD facility (PW-NM-SWD) from January 2020 to September 2020 to monitor the temporal change of PW quality (Point 2 in Fig. 1(a)). Along with these ten PW samples (PW-NM-SWD), ten Pecos River samples (RW-NM) were collected within the same period to characterize the background surface water quality (Point 2 in Fig. 1(a)). These temporal samples (ten PW-NM-SWD and ten RW-NM samples from Point 2 in Fig. 1(a)) were quantitatively analyzed for more than 300 targeted analytes, including wet chemistry, inorganics, radionuclides, organics such as VOCs, SVOCs, total petroleum hydrocarbons, organic acids, oil and grease, pesticides/herbicides, dioxins, and tentatively identified compounds. We also analyzed per- and polyfluoroalkyl substances (PFAS) in one PW-NM-SWD sample and one Pecos RW-NM sample. This is the first study that investigated PFAS in PW samples to the best of our knowledge. We also obtained data (wet chemistry and inorganics) from additional 22 PW samples from SWD wells (Points 1, 3, and 4 in Fig. 1(a)) and then combined all the data (in total 46 samples) for statistical analyses. This study is a first step toward a better understanding of PW quality in the Permian Basin; the objective of this study and our future research is to support the O&G industry, regulators, and stakeholders with information for risk-based assessment and designing optimal

methods for treatment and potential beneficial use of treated PW outside the O&G industry.

2. Materials and methods

2.1. Water sample collection

This study included 46 PW samples from the Permian Basin. Fig. 1(a) identifies sampling locations. Fig. 1(b) describes the TDS distribution for samples from each sampling point with mean, max, min, and standard deviation of TDS concentrations. Twenty-four PW samples (14 from the Delaware Basin in NM; and 10 from the Midland Basin in TX) were collected from unconventional reservoirs and analyzed by the authors. The information (wet chemistry and inorganics) for the other 22 PW samples was provided by industry collaborators in the Permian Basin. Samples were all from unconventional wells and collected from the wellhead, separator, PW storage tank/pond, and the back end of the SWD tank battery system. To track the temporal change of general water quality, ten PW-NM-SWD samples from the back end of a SWD tank battery system and ten Pecos RW-NM samples (Point 2 in Fig. 1(a)) were collected between January to September 2020 from the Delaware Basin (western subbasin of the Permian Basin), near Carlsbad, New Mexico.

Samples for wet chemistry, inorganic, and radionuclide analyses were collected in sterile plastic bottles. Samples for organic analyses were collected in method-specific bottles provided by the analytical laboratories. All samples were stored at 4 °C and transported to the labs on the same day under chain of custody. All sample collection, preservation, shipping, and analyses followed the United States Environmental Protection Agency (EPA) guidance and standard practices.

2.2. Wet chemistry, inorganic, and radionuclides analyses

Total dissolved solids (TDS) and total suspended solids (TSS) were measured by EPA standard methods 2540 C and 2540D (gravimetric method) using 0.15 µm filters. Total organic carbon (TOC) and dissolved organic carbon (DOC, using 0.45 µm filters) were measured using a TOC-V CSH Total Organic Carbon Analyzer (Shimadzu, Japan), following EPA method 415.3. The TOC procedure allows for removal of settleable solids and any free oil layer to prevent the clogging of valves, tubing, and injection needles. The suspended particles are included in the TOC measurement. pH was measured using a benchtop multi-parameter

meter (pH/con 300 Meter, Oakton Instruments, IL, USA). Ammonia was measured using a Hach DR6000 spectrophotometer with salicylate method 10031 (Hach, CO, USA). Chemical oxygen demand (COD) was measured using Hach COD test kits (Hach, CO, USA). Alkalinity was measured using Hach alkalinity test kits (Hach, CO, USA). Major anions were measured using ion chromatography (IC; Dionex ICS-2100, Thermo Fisher Scientific, CA, USA) following EPA method 300.0. Unfiltered, acidified water samples were used to measure the total metals and trace elements using an inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 4300 DV, PerkinElmer, MA, USA) and an inductively coupled plasma mass spectroscopy (ICP-MS; Elan DRC-e, PerkinElmer, MA, USA), using EPA method 200.7 and 200.8, respectively. Methylene blue active substances (surfactants) were analyzed based on EPA method 425.1. Radium-226 and Radium-228 were measured based on EPA methods 903.0 and 904.0, respectively, utilizing gamma spectroscopy. Gross Alpha and Gross Beta counts were based on EPA method 900.0.

2.3. Fluorescence excitation emission matrices (FEEM) analyses

FEEM was used to analyze the composition of dissolved organic matter (DOM) in the PW and river water samples. Spectra were obtained using a spectrofluorometer (Aqualog-UV-800-C, Horiba Instruments, NJ, USA). Excitation wavelengths were from 240 to 400 nm in 10 nm steps, and emission wavelengths were from 300 to 550 nm in 2 nm steps. Spectrum of deionized water at the wavelength of 350 nm was recorded as blank, and the equipment was auto zeroed before each analysis. In general, FEEM spectra can be divided into five regions (Jiang et al., 2020): Region I (Ex/Em 240–250/300–330 nm) and Region II (Ex/Em 240–250/330–380 nm): aromatic hydrocarbons; Region III (Ex/Em 240–250/380–550 nm): fulvic acid-like substances; Region IV (Ex/Em 250–400/300–380 nm): Microbial byproduct-like materials, such as carbohydrates, aldehydes, and alcohols; and Region V (Ex/Em 250–400/380–550 nm): humic acid-like organics. All spectra were corrected to 1 mg/L DOC using a suitable scale range.

2.4. Organic analyses

Organic analyses were performed by Eurofins Test America. Unfiltered water samples were collected in the method-specific bottles provided by the laboratory and shipped at 4 °C for analyses. VOCs were

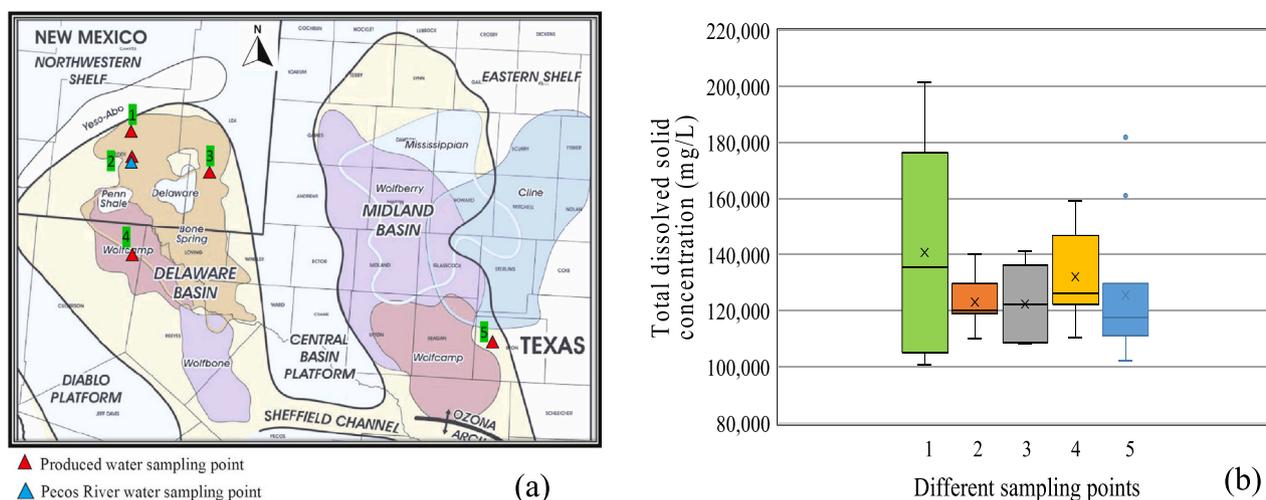


Fig. 1. (a) Sampling points of PW and Pecos River water in this study. (b) TDS distribution of PW at different sampling points. “x” represents Mean value, “—” from top to bottom represent Max, Median, and Min values, respectively. Two dots in Sampling Point 5 are outliers during the statistical analysis using the box and whisker plot. For PW samples: Point 1 (7 samples) TDS: 140,891 ± 38,516 mg/L; Point 2 (12 samples) TDS: 123,298 ± 8,752 mg/L; Point 3 (5 samples) TDS: 122,440 ± 14,217 mg/L; Point 4 (12 samples) TDS: 132,044 ± 15,933 mg/L; Point 5 (10 samples) TDS: 125,439 ± 25,368 mg/L. Detailed TDS data for each sampling point are in Data in Brief. Permian Basin County map is cited from (Shalexperts, 2021).

isolated via purge and trap, and SVOCs were subject to liquid-liquid extraction. They were analyzed using gas chromatography (GC, Agilent 6890) coupled with a quadrupole mass spectrometer (MS, Agilent 5973), following EPA method 8260 C and EPA method 8270D, respectively. Total petroleum hydrocarbons (TPH) and organic acids were analyzed using GC coupled with a flame ionization detector (Agilent 5890) following EPA method 8015D. Pesticides/herbicides were analyzed using GC (Agilent 5890) coupled with an electron capture detector following EPA method 8081B. PFAS were analyzed using solid-phase extraction and liquid chromatography-tandem mass spectrometry (LC/MS/MS, SCIEX 5500) following a modification of EPA method 537. The method detection limits and reporting limits for each PFAS in PW and river water samples are listed in Table 4. Dioxins analyses were performed via high-resolution GC/MS (Thermo DFS) in accordance with EPA method 1613B. Blank sample and external/internal standard calibration were used for quantification. Isotopic dilution was used to aid in quantitation for both PFAS and dioxin analyses.

3. Results and discussion

To check data quality in this study, charge balance (or anion-cation balance) was calculated for each sample, including samples measured by the authors and samples from other sources. All the samples had a percent error lower than 10%, except for three PW samples that had errors of 10.6%, 10.4%, and 11.0%, which might be caused by sample dilution factors and analytical errors when analyzing highly saline PW samples.

3.1. Chemical characterizations of PW samples

Tables 1 and 2 summarize the statistical results of general water quality parameters and element analyses (including radionuclides) of the total 46 PW samples. Detailed data for each sample can be found in Data in Brief. Concentrations of TDS, TOC, and ammonia have mean values of 128,423 mg/L, 104 mg/L, and 432 mg/L, respectively. These results are similar to previously reported PW quality from the Permian Basin (Jiang et al., 2021b; Rodriguez et al., 2020). TDS has a wide range from 100,000 to 201,000 mg/L, and the concentration of Cl^- and Na^+ (Table 2) correspond to 62.1% and 31.3 wt% of the TDS. These results are consistent with previous reports that nearly all basin waters with TDS concentrations above 10,000 mg/L are dominated by Na and Cl (Hanor, 1994) and that PW from the tight O&G plays is dominated by Na (median: 15,000–76,000 mg/L) and Cl (median: 22,000–150,000 mg/L) (Scanlon et al., 2020b). The median TDS in the Permian Basin (122,000 mg/L) is lower than in the Bakken tight oil (244,000 mg/L) and the Appalachian Basin Marcellus and Utica shale gas plays (166,000 mg/L) but higher than in the Eagle Ford shale play (57,000 mg/L) (Scanlon et al., 2020b).

TDS provides an indication of the PW mineral content, which is a major concern for PW management, treatment, and reuse. High salinity water corrodes metal pipes and tanks, which could be problematic for

PW transport, storage, and treatment. In addition, high concentrations of scale-forming ions, such as Ca^{2+} (mean concentration of 3821 mg/L), Mg^{2+} (745 mg/L), Sr^{2+} (450 mg/L), SO_4^{2-} (496 mg/L), and SiO_2 (108 mg/L), can cause scaling and decrease the performance of management/treatment systems. The SO_4^{2-} ion can also be reduced to H_2S by sulfate-reducing bacteria, which is a safety hazard to workers in addition to being corrosive.

High TDS limits the choice of treatment technologies. Reverse osmosis (RO) can be used to treat water with TDS < 30,000–45,000 mg/L (Chang et al., 2019). For unconventional PW with higher TDS concentration found across the Permian Basin, thermal techniques are required for treatment, such as thermal distillation and solar still (Chen et al., 2021; Liden et al., 2019, 2018). Resource and mineral recovery from PW has also been reported in a previous study which simultaneously recovered NH_4^+ , K^+ , and Mg^{2+} from PW by struvite precipitation after calcium pretreatment (Hu et al., 2021). Following mineral recovery, softened PW can be further treated for different fit-for-purpose applications.

PW may contain naturally occurring radioactive material (NORM), and the high concentration of Cl^- enhances the solubility of NORM (Fisher, 1998). Currently, there is limited data or information regarding the presence of NORM in Permian Basin PW. The ten PW-NM-SWD temporal samples from Sampling Point 2 (Fig. 1(a)) were analyzed for the NORM. Radium-226 + 228, uranium-234 + 238, thorium-228 + 230, polonium-210, and plutonium-238 were detected in the samples. In contrast, neptunium-237, americium-241, uranium-235, thorium-232, and plutonium-239 + 240 were not detected (Data in Brief). Ra-226 (half-lives of 1600 yr) and Ra-228 (half-lives of 5.75 yr) were chosen for comparison because they are the most abundant and most widely detected in other basins and represent the first soluble daughter product in the uranium-238 and thorium-232 decay chains, respectively. Results show total Ra (Ra-226 + Ra-228) has a mean level of 469.3 pCi/L (pico curies/L). As references, the results in this study are similar to a previous study for the Permian Basin (535 pCi/L), lower than other major O&G production basins such as Marcellus shale (median: 1980 pCi/L) and Bakken (1200 pCi/L), and higher than Eagle Ford (284 pCi/L) (Scanlon et al., 2020b). These results also show a large temporal variance between PW samples from 2.56 to 576 pCi/L for Ra-228 and from 0.74 to 970 pCi/L for Ra-226 in Sampling Point 2.

While the focus is primarily on the quantitation of Ra-226 and Ra-228, both exist as parts of the uranium-238 and thorium-232 decay chains, respectively. Parent and daughter isotopes have been identified in PW, although the various long-lived parent products (e.g., thorium-230 and thorium-228, respectively) are largely insoluble and both decay into gases (radon-222 and radon-224), which can be transported elsewhere.

Table 1
Statistical results of general quality parameters of the total 46 PW samples.

		Mean	Max	Min	25th percentile	50th percentile	75th percentile
Alkalinity	mg/L as CaCO_3	272	870	100	128	207	336
Ammonia	mg/L	432	750	320	330	400	495
COD	mg/L	1626	3100	930	1250	1400	1950
pH	SU	6.6	8.1	3.9	6.3	7.0	7.0
TDS	mg/L	128,641	201,474	100,830	113,441	122,280	134,525
TOC	mg/L	103.5	248.1	2.4	28	90.6	173.3
TSS	mg/L	342.9	790	85	142.5	375	422.5
Turbidity	NTU	116.4	200	23	36	110	200
MBAS	mg/L	1.10	2.1	0.047	0.92	0.97	1.33

Note: COD: Chemical Oxygen Demand; TDS: Total Dissolved Solids; TOC: Total Organic Carbon; TSS: Total Suspended Solids; MBAS: Methylene Blue Active Substances.

Table 2
Statistical results of comprehensive elements analyses of the 46 PW samples.

		Mean	Max	Min	25th percentile	50th percentile	75th percentile
Cations							
Aluminum	mg/L	1.09	3.95	0.37	0.63	0.76	1.25
Arsenic	mg/L	3.17	6.04	1.62	1.74	2.64	4.61
Barium	mg/L	2.21	12.00	0.10	0.45	1.69	3.00
Beryllium	mg/L	0.03	0.04	0.01	0.01	0.03	0.04
Bismuth	mg/L	1.02	1.77	0.71	0.72	0.81	1.55
Boron	mg/L	42.34	76.50	17.20	33.29	40.65	51.03
Cadmium	mg/L	0.47	0.81	0.04	0.08	0.63	0.77
Calcium	mg/L	3821	8186	880	1705	3531	5744
Chromium	µg/L	1.7	2.2	1.3	1.3	1.6	2.2
Cobalt	µg/L	7.7	7.8	7.5	7.5	7.7	7.8
Copper	mg/L	0.65	1.46	0.24	0.24	0.45	1.26
Ferrous iron	mg/L	3.09	6.70	0.57	0.73	3.00	5.50
Iron	mg/L	19.35	65.20	0.50	4.60	14.00	25.70
Lithium	mg/L	22.39	52.28	11.74	20.00	21.02	23.40
Magnesium	mg/L	745.0	1877	295.3	472.7	621.3	959.1
Manganese	µg/L	488	1239	10	116	427	781
Molybdenum	mg/L	0.21	0.38	0.10	0.11	0.18	0.35
Potassium	mg/L	923	3637	222	449	808	1171
Selenium	mg/L	2.5	2.5	2.5	n/a	2.5	n/a
Silica	mg/L	107.7	195.4	4.0	29.2	115.7	178.2
Sodium	mg/L	40,896	68,985	25,080	37,000	39,673	42,967
Strontium	mg/L	449.9	1404	28.9	116.4	325.3	816.5
Thallium	mg/L	0.83	0.84	0.82	n/a	0.83	n/a
Thorium	mg/L	0.048	0.054	0.035	0.035	0.054	0.054
Uranium	mg/L	0.303	0.5	0.19	0.19	0.22	0.5
Vanadium	µg/L	79.6	94.5	61.4	61.4	83.0	94.5
Zinc	mg/L	1.14	1.81	0.17	0.17	1.45	1.81
Anions							
Sulfate	mg/L	496	965	151	243	510	690
Phosphorus as P	mg/L	8.5	36.0	1.7	2.5	6.4	8.9
Nitrite as N	mg/L	n/a	16	n/a	n/a	n/a	n/a
Iodide	mg/L	88	94	77	82	90	94
Chloride	mg/L	78,648	120,200	57,543	69,269	75,658	86,979
Bromide	mg/L	431	960	95	238	289	608
Radionuclides							
Gross Alpha	pCi/L	1105.6	1630	660	745	863	1630
Gross Beta	pCi/L	874.6	1230	456	748	889	1050
Radium-226	pCi/L	237.6	970.0	0.7	19.1	72.8	415.5
Radium-228	pCi/L	231.7	576.0	2.6	137.5	273.0	285.0
Uranium-234	pCi/L	0.33	0.76	0.20	0.24	0.24	0.24
Uranium-238	pCi/L	0.17	0.17	0.17	n/a	n/a	n/a
Thorium-228	pCi/L	21.5	52.1	3.4	3.7	21.5	30.5
Thorium-230	pCi/L	0.22	0.39	0.09	0.17	0.21	0.24
Polonium-210	pCi/L	3.28	5.38	1.75	2.24	2.72	4.05
Plutonium-238	pCi/L	0.17	0.17	0.17	n/a	n/a	n/a

Note: n/a: not available.

3.2. Dissolved organic matter (DOM) in PW-NM-SWD characterized by FEEM analyses

It is costly and time-consuming to analyze the whole profile of organic compounds in PW samples because they contain numerous anthropogenic and natural organics (Section 3.3). 3D-FEEM can provide pragmatic information for the DOM in PW based on the phenomenon that a large portion of organic compounds, such as proteins and bacterial metabolites (fulvic and humic substances), have fluorescent emission characteristics (Jiang et al., 2021a). Although FEEM lacks quantitative information on specific compounds, it provides low cost and real-time results compared to GC/LC-MS, and the advantages of higher selectivity and a wider range compared to conventional fluorescence.

In this study, FEEM was used to characterize DOM in three PW-NM-SWD samples collected from three different SWD facilities in the Delaware Basin and one Pecos RW-NM sample from Carlsbad, NM (all samples were collected from Sampling Point 2 in Fig. 1(a)). All three PW samples have similar peaks in regions I, II, III, and IV (Fig. 2). However, intensities varied between peaks. PW3 has more peaks compared to PW1 and PW2. PW1 and PW2 have the strongest peaks in region IV, indicating a high concentration of microbial byproduct-like materials associated with the activity of microbial metabolism. If these PWs are to be

reused for HF, more biocides may be required. PW3 has the strongest peak in regions I, II, III, and IV that represent high concentrations of aromatic hydrocarbon, fulvic acid-like substances, and microbial byproduct-like materials (Dahm et al., 2013). PW1 and PW2 showed relatively lower peak intensity in region III, fulvic acid-like substances. All samples had low-intensity peaks in region V, which are humic acid-like materials. Such quick FEEM analyses could be performed in a field lab as a real-time indicator of organic substances and petroleum hydrocarbons to assist in on-site evaluation of PW treatment performance. The Pecos River sample showed much lower intensity (0–0.025) of DOM compared with PW samples (0–0.7). The major peaks for the Pecos River sample represent aromatic carbon (regions I and II) and fulvic acid-like substances (region III).

The FEEM results, however, do not provide more information regarding the specific organic compounds and their quantity. Some compounds may cause negative environmental and health impacts in very low concentrations. Thus, targeted organic compound analyses were performed in this study to investigate the organic profile in PW samples.

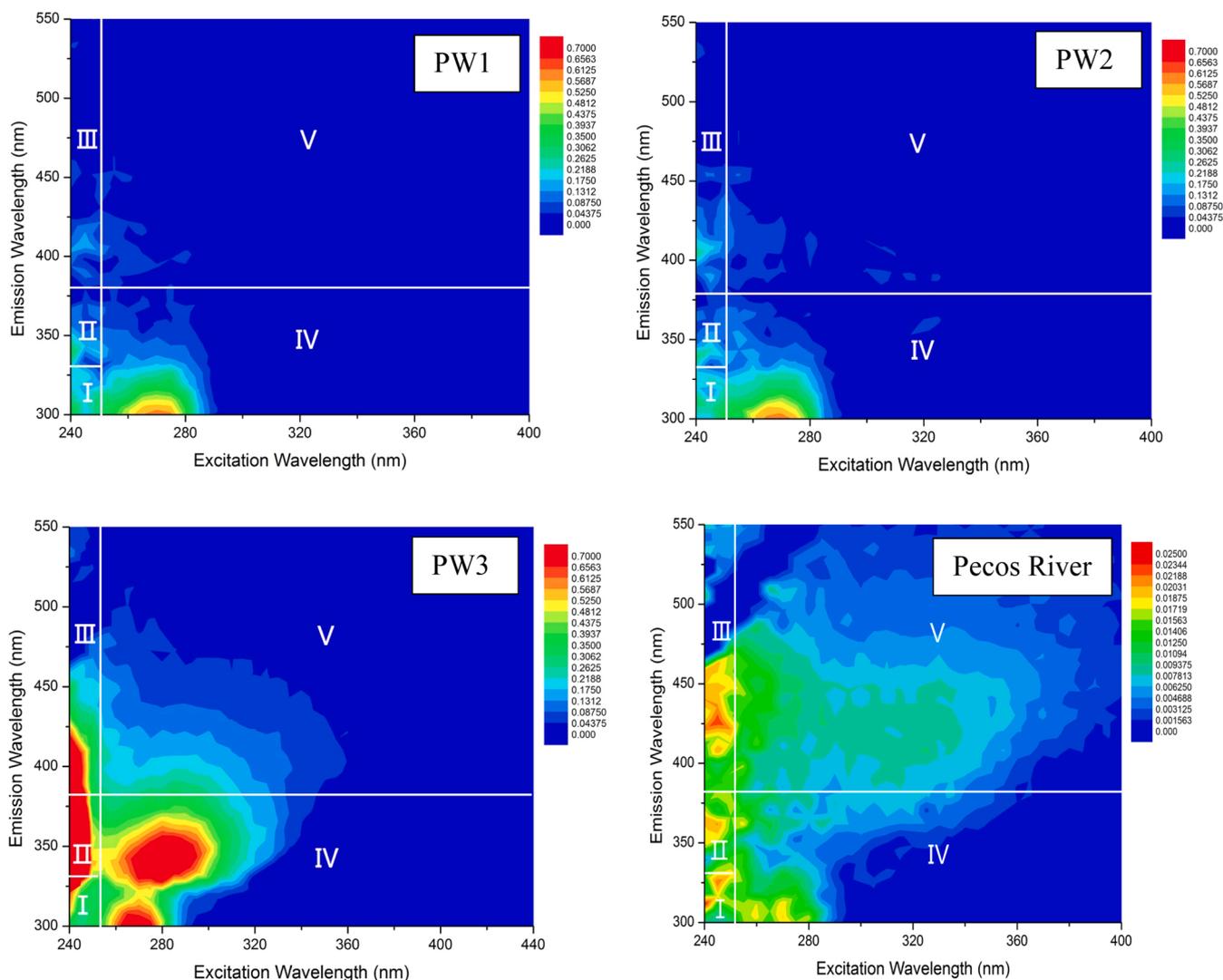


Fig. 2. FEEM spectra of three PW-NM-SWD samples from the Delaware Basin and one Pecos RW-NM sample from Carlsbad, New Mexico. All spectra are normalized to 1 mg/L DOC with a suitable scale for fluorescence intensity (PW: 0–0.7; Pecos RW: 0–0.025).

3.3. Target organic analyses

As discussed in Sections 2.4 and 3.2, advanced analytical instruments/methods were used for the targeted analysis of organic compounds in the ten temporal PW-NM-SWD samples from Sampling Point 2 in Fig. 1(a). In summary, 28 organic compounds, PFAS, diesel range organics (DRO), gasoline range organics (GRO), and motor oil range organics (MRO), were quantitatively identified in these PW-NM-SWD samples, while other 218 constituents were not detected. The list of undetected compounds can be found in Data in Brief.

Table 3 shows the statistical results of organic compounds quantified during the analyses of the ten PW-NM-SWD samples. Detected VOCs of high relative abundances include benzene (min – max: 1900 – 4900 $\mu\text{g/L}$), toluene (1700 – 3700 $\mu\text{g/L}$), ethylbenzene (72 – 160 $\mu\text{g/L}$), and xylene (710 – 1600 $\mu\text{g/L}$). Results are consistent with other studies and are anticipated because these compounds are closely related to O&G production (Lester et al., 2015). BTEX constituents usually have the highest concentrations during the HF flowback period (Luek and Gonsior, 2017). No other VOCs were detected, which may be because samples were collected at an SWD, and volatilization might occur during transportation (piping and trucking) and storage before sampling.

For general SVOCs, phenol (170–250 $\mu\text{g/L}$) and pyridine (120–300 $\mu\text{g/L}$) have the highest relative abundances. Phenol has been

reported as being used in HF fluid to help coat sand proppants and as a disinfectant to eliminate bacteria (Jackson, 2014). The leaching of phenol and formaldehyde (detected in the range of 53–210 $\mu\text{g/L}$ in this study) depends on the temperature in the formation (Mazero, 2013; Schenk et al., 2019). Pyridine is the most frequently detected SVOC in HF fluids, which may be due to its use as a precursor for one of the HF additives (U.S.EPA, 2011), and it has been reported as naturally occurring in oil shales (Roper, 1992). Alcohols are also used for several functions in HF fluids, production chemistry, and SWD treatment chemistry. They are routinely used as solvents, surfactants, gelling agents, friction reducer, and corrosion inhibitors. This study detected the mostly frequently used alcohols including methanol (5.6–52 mg/L), ethanol (0.14–0.98 mg/L), ethylene glycol (ND–27 mg/L), and phenols (FracFocus, 2021). The alcohols detected in this study are likely from production and SWD treatment chemistry, not HF chemistry. Other SVOCs such as 1,4-dioxane (ND – 21 $\mu\text{g/L}$), 1-methylnaphthalene (15–36 $\mu\text{g/L}$), and 2,4-dimethylphenol (29–42 $\mu\text{g/L}$) were detected in this study and reported in other studies (Luek and Gonsior, 2017).

Biocides are often added to HF fluids and fluids associated with production operation for unconventional O&G development and SWD treatment to inactivate bacteria that are ubiquitous in the environment and cause problems during HF, including biofouling, production of toxic H_2S , and corrosion of metal equipment (Jiang et al., 2021a). In this

Table 3
Statistical results of the detected organic compounds in the ten PW-NM-SWD samples.

		Mean	Max	Min	25th percentile	50th percentile	75th percentile
VOC							
Benzene	µg/L	2611.1	4900	1900	2200	2200	2600
Ethylbenzene	µg/L	112.2	160	72	93	110	130
Toluene	µg/L	2533	3700	1700	2000	2400	2900
Xylenes, Total	µg/L	1185.6	1600	710	1100	1300	1400
SVOC - General							
1,1'-Biphenyl	µg/L	5.9	8.5	3.8	4.6	5.2	7.2
1,4-Dioxane	µg/L	n/a	21	ND	n/a	n/a	n/a
1-Methylnaphthalene	µg/L	22.7	36	15	18	21	26
2-Methylnaphthalene	µg/L	38.3	65	26	29	36	45
2-Methylphenol	µg/L	81.8	98	68	77	80	85
2,4-Dimethylphenol	µg/L	34.1	42	29	31.5	33	36
Ethylene glycol	mg/L	n/a	27	ND	n/a	27	n/a
Ethanol	mg/L	0.51	0.98	0.14	0.21	0.57	0.67
Methanol	mg/L	24.5	52	5.6	12	26	27
Methylphenol, 3 & 4	µg/L	90.4	110	72	85	91	96
Phenol	µg/L	203.3	250	170	170	210	220
Pyridine	µg/L	237.5	300	120	235	240	260
Pesticides/Herbicides							
alpha-BHC (benzene hexachloride)	µg/L	0.018	0.027	0.009	n/a	n/a	n/a
Endosulfan I	µg/L	0.855	0.98	0.73	n/a	n/a	n/a
Endrin	µg/L	n/a	0.004	ND	n/a	0.004	n/a
Organic Acids							
Acetic acid	mg/L	n/a	89	n/a	n/a	n/a	n/a
Butyric acid	mg/L	n/a	7.1	n/a	n/a	7.1	n/a
Propionic acid	mg/L	n/a	5.7	n/a	n/a	5.7	n/a
SVOC-PAH							
Anthracene	µg/L	n/a	1.1	ND	n/a	n/a	n/a
Naphthalene	µg/L	15	24	11	12	16	16
Phenanthrene	µg/L	3.76	6.6	2.7	3.18	3.4	4.03
Fluorene	µg/L	4.35	5.6	3.1	n/a	4.7	n/a
Carbonyl Compounds							
Formaldehyde	mg/L	0.14	0.21	0.053	0.11	0.15	0.18
SVOC-TPH							
n-Decane	µg/L	556.7	890	340	390	530	610
Oil and Grease							
DRO (C10-C20)	mg/L	49	130	22	26	35	52
GRO (C6-C10)	mg/L	23.5	46	13	15	19.5	28
MRO (C20-C34)	mg/L	32.4	97	12	16	26	32
Tributyl phosphate	µg/L	34.6	74	3.3	12	30.5	53
Tentatively Identified Compounds (TIC)	µg/L	531.1	1000	280	320	350	840

Note: n/a: data not available; ND: not detected. PAH: polycyclic aromatic hydrocarbon; TPH: total petroleum hydrocarbons; DRO: diesel range organics; GRO: gasoline range organics; MRO: motor oil range organics.

study, the commonly used biocides, including quaternary ammonium chloride and glutaraldehyde for HF (FracFocus, 2021), were not detected. Detected biocides at very low concentrations include three organochloride insecticides: alpha-benzene hexachloride (0.009 – 0.027 µg/L), endosulfan I (0.73 – 0.98 µg/L), and endrin (ND – 0.004 µg/L). Reasons for these results may include, firstly, the biocides can react with microbes and other chemicals during the HF and be degraded to other organic compounds. Secondly, biocides can undergo chemical changes in the subsurface, which has different temperatures, salinity, and pH. A study simulated the transformation of glutaraldehyde during HF and found that the fate of glutaraldehyde depended on downhole conditions. It can undergo rapid auto-polymerization and sorb onto shale and then remain underground, or it can remain stable and return to the surface with a half-life of 20 days (Kahrilas et al., 2016). Thirdly, samples collected in this study were mainly PW, in which biocides may have a lower concentration than in HF flowback water.

Acids are used as iron controllers and pH adjusting agents during O&G production. This study found the concentrations of organic acids were highly variable from non-detect to a maximum concentration of 89 mg/L for acetic acid, 7.1 mg/L for butyric acid, and 5.7 mg/L for propionic acid. They may correspond with SWD treatment chemistry. However, it may also come from anaerobic microbial metabolism by degrading the biopolymers during HF (Olsson et al., 2013) or degradation of organic matter in the reservoir at temperatures above 80 °C

(Carothers and Kharaka, 1978). Better control of bacteria in PW may decrease the concentrations organic acids.

Polycyclic aromatic hydrocarbons (PAHs) are a large class of cancer-causing chemicals and occur naturally in coal, crude oil, and gasoline. They have been quantitatively reported in several studies, including in Denver-Julesburg Basin flowback samples (Lester et al., 2015) and in Marcellus PW samples (Jackson, 2014). According to the United States Centers for Disease Control and Prevention, the health effects of people exposed to low levels of PAHs are unknown; large amounts of PAHs can cause blood and liver abnormalities (Centers for Disease Control and Prevention, 2019). The PAHs detected in this study are in low µg/L range, including anthracene (min – max: ND – 1.1 µg/L), naphthalene (11 – 24 µg/L), phenanthrene (2.7 – 6.6 µg/L), and fluorene (3.1 – 5.6 µg/L). As anticipated for PW samples, oil and grease were detected in relatively high concentrations in the PW samples with diesel range organics (22 – 130 mg/L), gasoline range organics (13 – 46 mg/L), and motor oil range organics (12 – 97 mg/L).

Tentatively identified compounds (TICs) with a mean of 531 µg/L were detected in the PW-NM-SWD samples. TIC refers to a compound that can be detected by the analysis method, but its identity cannot be confirmed without further investigation. All VOC and SVOC samples analyzed by the commercial laboratory were subject to TIC searches using the National Institute of Standards and Technology (NIST) mass spectra library, which consists of hundreds of thousands of identified compounds. To improve hazard and risk assessment, and reduce concern

for reuse of treated PW, an effort should be made to identify compounds of concern within this unresolved fraction (U.S.EPA, 2020). A TIC can be converted to a target analyte if the method is developed to include the compound. This can be done by including reference standards for the chemical in calibration and quality control samples. Our future research will focus on the non-target analysis of these unknown chemicals in raw/untreated and treated PW using high-resolution LC/MS.

3.4. PFAS analyses

PFAS have been widely used in a variety of consumer products and in industrial applications. At the time of this study, they are considered recalcitrant in the environment due to the limited and/or slow breakdown of the perfluorocarbon moieties although additional research is ongoing (Ghisi et al., 2019). Further, PFAS can accumulate or concentrate in the environment and may have the potential to cause adverse health effects (Kwiatkowski et al., 2020). The U.S. EPA established the lifetime health advisory levels at 70 ng/L for combined perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) concentrations in the drinking water (U.S.EPA, 2016). Currently, there is limited testing of PFAS in public water sources in the Permian Basin, and no published study investigated PFAS in PW to the best of our knowledge. Hence, PFAS analyses were performed on one PW-NM-SWD sample from an SWD facility in Sampling Point 2 (Fig. 1(a)) and one Pecos RW-NM sample (Table 4). Despite the limited sample size, this is the first step towards the characterization of PFAS in PW and Pecos River water.

For the analyses, each sample was spiked with isotopically labeled homologs of target analytes to monitor matrix interference, extraction efficiency, and analytical precision and accuracy. For the data reported, there is a difference between reporting limits (RL) and method detection limits (MDL). The RL generally corresponds with the lowest range of calibration, while the MDL is a statistical calculation of the lowest possible concentration that can be detected above background noise. Detections above the MDL but below the RL are designated with a “J”

flag to indicate that the value is an estimate since it is below the lowest point of the calibration curve.

There is also a need to analyze method blank and laboratory control samples because of the potential for trace level detection of the PFAS, even with reagent-grade purified water in cleanroom conditions. If results were detected above the RL, the entire analytical batch would have to be re-extracted. If method blanks and/or laboratory control samples were detected, even with a J flag value (i.e., MDL < detection < RL), samples associated with this analytical batch that were detected for the same analytes were designated with a “B” flag to denote potential detection in a blank.

In total 34 PFAS compounds were analyzed in this study (Table 4). Five PFAS compounds were detected in the PW sample including PFBS (0.17 J ng/L, full names are listed in Table 4 note), PFBA (0.31 J B ng/L), PFHxS (0.25 J B ng/L), NETFOSE (0.98 J ng/L), and PFTeA (0.24 J ng/L). These PFAS were estimated in very low concentrations with “J” flag values - slightly above MDL but below RL. In addition, PFBA and PFHxS had estimated values with a “B” flag, indicating they were detected in the blank samples.

More PFAS compounds were detected in the Pecos RW-NM sample (10 compounds) and at higher concentrations than the PW-NM sample (5 compounds). PFAS detected in the Pecos River sample include PFBS (2.0 ng/L), PFBA (1.3 J B ng/L), PFHpA (0.35 J ng/L), PFHxS (1.0 J B ng/L), PFHxA (1.2 J ng/L), FOSA (0.54 J B ng/L), PFOS (1.2 J ng/L), PFOA (1.0 J ng/L), PFPeS (0.24 J ng/L), and PFPeA (1.8 ng/L). In general, trace PFAS may be expected in the Pecos River samples as these compounds are ubiquitous in the environment. It is not expected to find PFAS in the formation water that has been geologically sequestered from synthetic organic chemicals. According to the FracFocus, no PFAS were used in HF chemical additives in the Permian Basin (FracFocus, 2021). However, fluoropolymers and fluorinated surfactants are reported in FracFocus for HF in the Permian Basin and other basins (FracFocus, 2021). Identification of these substances is challenging due to trade secret or proprietary information; further non-target and target analytical methods can be utilized to characterize these substances in PW.

Table 4
PFAS analyses results of a PW-NM-SWD and a Pecos RW-NM sample (unit: ng/L).

	PW/ Pecos	PW MDL/RL	Pecos MDL/RL		PW/ Pecos	PW MDL/RL	Pecos MDL/RL
PFBS	0.17 J/2.0	0.15/1.5	0.16/1.6	PFNS	ND/ND	0.12/1.5	0.13/1.6
PFBA	0.31 J B/ 1.3 J B	0.25/1.5	0.28/1.6	PFNA	ND/ND	0.2/1.5	0.21/1.6
PFDS	ND/ND	0.23/1.5	0.25/1.6	FOSA	ND/ 0.54 J B	0.25/1.5	0.28/1.6
PFDA	ND/ND	0.23/1.5	0.24/1.6	PFOS	ND/1.2 J	0.39/1.5	0.42/1.6
PFDoS	ND/ND	0.33/1.6	0.35/1.6	PFOA	ND/1.0 J	0.62/1.5	0.67/1.6
PFDoA	ND/ND	0.4/1.6	0.43/1.6	PFPeS	ND/0.24 J	0.22/1.5	0.24/1.6
PFHpS	ND/ND	0.14/1.6	0.15/1.6	PFPeA	ND/1.8	0.36/1.5	0.39/1.6
PFHpA	ND/0.35 J	0.18/1.5	0.2/1.6	PFTeA	0.24 J/ND	0.21/1.5	0.23/1.6
PFHxS	0.25 J B/ 1.0 J B	0.12/1.5	0.13/1.6	PFTriA	ND/ND	0.94/1.5	1/1.6
PFHxA	ND /1.2 J	0.42/1.5	0.46/1.6	PFUnA	ND/ND	0.8/1.5	0.87/1.6
NETFOSA	ND/ND	0.63/1.5	0.68/1.6	NMeFOSA	ND/ND	0.31/1.5	0.34/1.6
NETFOSE	0.98 J/ND	0.62/1.5	0.67/1.6	NMeFOSAA	ND/ND	2.3/15	2.4/16
NETFOSAA	ND/ND	1.4/15	1.5/16	NMeFOSE	ND/ND	1/2.9	1.1/3.1
4:2 FTS	ND/ND	3.8/15	4.1/16	6:2 FTS	ND/ND	1.5/15	1.6/16
8:2 FTS	ND/ND	1.5/15	1.6/16	10:2 FTS	ND/ND	0.14/1.5	0.15/1.6
DONA	ND/ND	0.13/1.5	0.14/1.6	HFPO-DA (GenX)	ND/ND	1.1/2.9	1.2/3.0
F-53B Major	ND/ND	0.17/1.5	0.19/1.6	F-53B Minor	ND/ND	0.23/1.5	0.25/1.6

Note: ND: not detected; MDL: minimal detection limit (U.S.EPA, 2022); RL: reporting limit.

J: below reporting limit but above minimal detection limit; B: potential blank contamination.

PFBS: Perfluorobutanesulfonic acid; PFBA: Perfluorobutanoic acid; PFDS: Perfluorodecanesulfonic acid; PFDA: Perfluorodecanoic acid; PFDoS: Perfluorododecanesulfonic acid; PFDoA: Perfluorododecanoic acid; PFHpS: Perfluoroheptanesulfonic acid; PFHpA: Perfluoroheptanoic acid; PFHxS: Perfluorohexanesulfonic acid; PFHxA: Perfluorohexanoic acid; PFNS: Perfluorononanesulfonic acid; PFNA: Perfluorononanoic acid; FOSA: Perfluorooctanesulfonamide; PFOS: Perfluorooctanesulfonic acid; PFOA: Perfluorooctanoic acid; PFPeS: Perfluoropentanesulfonic acid; PFPeA: Perfluoropentanoic acid; PFTeA: Perfluorotetradecanoic acid; PFTriA: Perfluorotridecanoic acid; PFUnA: Perfluoroundecanoic acid; NETFOSA: N-ethyl perfluorooctane sulfonamide; NMeFOSA: N-methyl fluorooctane sulfonamide; NETFOSE: N-ethyl perfluorooctane sulfonamido ethanol; NMeFOSAA: N-Methylperfluorooctane sulfonamidoacetic acid; NETFOSAA: N-ethyl perfluorooctanesulfonamidoacetic acid; NMeFOSE: N-methyl perfluorooctane sulfonamidoethanol; 4:2 FTS: 4:2 Fluorotelomer sulfonic acid; 6:2 FTS: 6:2 Fluorotelomer Sulfonate; 8:2 FTS: 8:2 Fluorotelomer sulfonic acid; 10:2 FTS: 10:2 Fluorotelomer sulfonic acid; DONA: 4,8-dioxo-3 h-perfluorononanoic acid; PO-DA (GenX): 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate; F-53B Major: 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate; F-53B Minor: 11-Chlororeicosafuoro-3-oxaundecane-1-sulfonic acid.

It should be noted that the PFAS data presented in this study were estimated using only one PW sample collected from an SWD facility and one river water sample. More analyses of diverse samples are needed to identify the spatial and/or temporal variability. It is also important to elucidate the sources of PFAS in PW with the elimination of any potential cross-contamination during PW transportation in pipelines, trucking, storage, sampling, or a legacy from the source water introduced into the formation during fracturing.

3.5. Temporal variability of PW-NM-SWD water quality

Fig. 3 shows the temporal change of the major constituents in the Permian Basin PW-NM-SWD samples in 2020. The means and relative standard deviations (RSD) for the major constituents are TDS (122,500 mg/L and 7.6%), alkalinity (129 mg/L as CaCO₃ and 12.1%), Na⁺ (35,000 mg/L and 4.9%), Cl⁻ (78,200 mg/L and 9.3%), Ca²⁺ (5800 mg/L and 13.1%), and SO₄²⁻ (528.6 mg/L and 17.2%). Results show a stable trend for the major constituents except for the SO₄²⁻, which may be related to bacterial activity and sulfate mineral solubility (or scaling potential) in PW. Tracking the quality change would assist operators in evaluating process performance. With more data collected, machine learning techniques, such as time series analysis, can be used to predict the water quality to assist downstream companies or treatment facilities to better treat the PW and prevent unanticipated events (Jiang et al., 2021b).

3.6. Analyses of the nearby river water (RW-NM)

Discharge or reuse of treated PW outside the O&G field is not presently permitted in the Permian Basin. Characterization of water quality of nearby water bodies provides background analytical information and baseline data for potential discharge and reuse of treated PW. Tables 5–7 summarize the statistical results for the analyses of ten Pecos RW-NM samples (01/2020–09/2020); PFAS analyses are shown in Table 4. Detailed information for each sample can be found in Data in Brief (Pecos River). Fig. 4 shows the temporal change of major constituents in the Pecos River samples in 2020. Results show the quality of Pecos River samples varied seasonally with means and RSDs for the major constituents are TDS (4591 mg/L and 17.7%), alkalinity (140.8 mg/L as CaCO₃ and 14.6%), Na⁺ (881 mg/L and 29.3%), Cl⁻ (1453 mg/L and 17.3%), Ca²⁺ (570 mg/L and 19.5%), and SO₄²⁻ (1720.5 mg/L and 17%). There are multiple possible sources that may contribute to the variations in

salinity in the river such as PW and shallow brines that are known to be presented across much of the region.

To distinguish between various potential Na⁺ and Cl⁻ sources to the Pecos, Na-Cl-Br systematics were utilized (Fig. 5). Most unconventional oil and gas formations in the basin contain ancient, evaporated seawater that exhibits a particular relationship between ratios of Br⁻, Cl⁻, and Na⁺ concentrations, depending on the degree of local evaporation that occurred in the geologic past (Engle et al., 2016; Nicot et al., 2020). Conversely, shallow brine that gains its salinity from the dissolution of halite follows a different trajectory, depending on the degree of dissolution (Engle et al., 2016). Fig. 5 compares isometric log-ratio transformed Na, Cl, and Br data (see (Engle and Rowan, 2013) for further details) of samples from the Permian Basin PW, the Pecos River, and four shallow brine samples from immediately above the salt layers in the Rustler aquifer, near Carlsbad, New Mexico (Siegel et al., 1991). The data are compared against modeled pathways for ancient seawater evaporation and halite dissolution as described in Engle et al. (2016). Correspondence between Pecos River samples and shallow brine from the Rustler aquifer (located stratigraphically above the O&G producing formations) suggest that shallow brines from evaporite mineral dissolution are the dominant source of salinity to the Pecos River samples. A potential reason for the increasing salinity in the Pecos River observed in the data is from widespread groundwater withdrawal due to severe droughts in the region, allowing for upward migration of shallow brines.

Radionuclides were detected in the river samples (Table 6). The combined Ra-226 and Ra-228 activity was measured as 3.98 pCi/L, below the maximum contaminant level (MCL) of EPA's regulation (5 pCi/L) for drinking water. However, the maximum of Ra-226 reached 29.9 pCi/L during the monitoring, reflecting that Ra-226 activity in the Pecos River can pass the regulatory limit at some point, which indicates more measurements and treatment are required for safe use of Pecos River water. Gross Beta is 14.08 pCi/L, below the MCL of 50 pCi/L; however, Gross Alpha of 24.6 pCi/L exceeded the MCL of 15 pCi/L.

There are fewer organic compounds detected in Pecos RW-NM samples (6 compounds) compared with PW-NM-SWD samples (28 compounds). Table 7 shows the quantified organics while the undetected compounds can be found in Data in Brief. No VOCs were found in the Pecos River, which is reasonable because of their volatile nature. Other detected organics, including pesticides (endosulfan I: 0.004 – 0.004 µg/L, 4,4'-DDD: ND – 0.01 µg/L, and 4,4'-DDT: ND – 0.006 µg/L), PAHs (naphthalene: ND – 6 µg/L and fluorene: ND – 1.2 µg/L), and dioxins (2,3,7,8-tetrachlorodibenzodioxin, ND – 0.14 pg/L), were in low

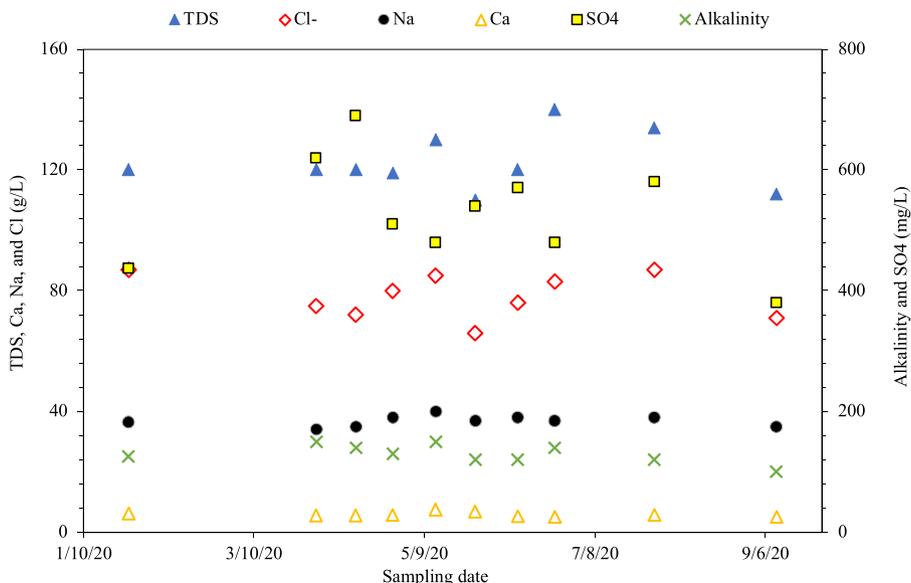


Fig. 3. Temporal change of the major constituents in ten Permian Basin PW-NM-SWD samples.

Table 5
Statistical results of general quality parameters of the Pecos RW-NM samples.

		Mean	Max	Min	25% percentile	50% percentile	75% percentile
Alkalinity	mg/L	140.8	170	118	120	135	162.5
Ammonia	mg/L	0.15	0.2	0.12	0.13	0.14	0.17
TDS	mg/L	4591	6200	3210	4125	4550	5050
TOC	mg/L	4.2	12.3	1.9	2.3	3.1	4.7
TSS	mg/L	43	57	26	32	45	54
Turbidity	NTU	7.5	16.0	1.1	3.9	6.7	11.5
COD	mg/L	28	39	13	22	30	35
Nitrate as N	mg/L	1.2	1.8	0.7	0.8	1.1	1.6
Nitrite as N	mg/L	0.2	0.2	0.2	n/a	0.2	n/a
pH	SU	8.1	8.2	7.7	8.0	8.1	8.2
SAR		8.5	11.8	5.6	n/a	8.4	n/a
MBAS	mg/L	0.07	0.12	0.04	0.05	0.06	0.08

Note: n/a: data not available. COD: Chemical Oxygen Demand; TDS: Total Dissolved Solids; TOC: Total Organic Carbon; TSS: Total Suspended Solids; SAR: sodium adsorption ratio; MBAS: Methylene Blue Active Substances.

Table 6
Statistical results of comprehensive elements analyses of the Pecos RW-NM samples.

		Mean	Max	Min	25% percentile	50% percentile	75% percentile
Cations							
Aluminum	µg/L	84	84	84	n/a	84	n/a
Arsenic	µg/L	26	26	26	n/a	26	n/a
Barium	µg/L	27	38	18	24	25	32
Boron	µg/L	271	271	271	n/a	271	n/a
Cadmium	µg/L	0.4	0.8	0.0	n/a	0.4	n/a
Calcium	mg/L	570.2	820.0	402.0	512.5	555.0	615.0
Chromium	µg/L	3.2	3.2	3.2	n/a	3.2	n/a
Cobalt	µg/L	5.1	5.1	5.1	n/a	5.1	n/a
Iron	µg/L	518	890	190	270	510	759
Lead	µg/L	1.1	1.1	1.1	n/a	1.1	n/a
Lithium	µg/L	95.2	140.0	58.4	80.8	96.0	110.0
Magnesium	mg/L	150.0	150.0	150.0	n/a	150.0	n/a
Manganese	µg/L	17.1	17.6	16.6	n/a	17.1	n/a
Mercury	µg/L	0.2	0.2	0.2	n/a	0.2	n/a
Molybdenum	µg/L	2.7	2.9	2.4	2.4	2.7	2.9
Potassium	µg/L	8.2	12.0	5.9	7.1	7.8	9.3
Selenium	mg/L	8.2	16.2	2.2	2.2	6.2	16.2
Silica	mg/L	12.9	12.9	12.9	n/a	12.9	n/a
Sodium	mg/L	881	1400	520	668	870	983
Strontium	mg/L	9.5	14.0	5.9	8.8	9.4	10.1
Uranium	µg/L	6.0	6.0	6.0	n/a	6.0	n/a
Vanadium	µg/L	35.6	35.6	35.6	n/a	35.6	n/a
Anions							
Chloride	mg/L	1454	1700	936	1200	1600	1600
Sulfate	mg/L	1721	2100	1205	1475	1750	2000
Fluoride	mg/L	0.7	0.9	0.5	0.7	0.8	0.8
Bromide	mg/L	0.7	0.8	0.5	0.6	0.7	0.8
Radionuclides							
Gross Alpha	pCi/L	24.6	39.8	7.7	12.9	27.4	35.1
Gross Beta	pCi/L	14.1	24.2	1.4	4.2	14.6	23.8
Radium-226	pCi/L	0.3	1.1	0.1	0.1	0.2	0.3
Radium-228	pCi/L	3.4	29.9	0.2	0.3	0.4	0.6
Uranium-234	pCi/L	6.6	7.6	5.5	n/a	6.6	n/a
Uranium-235	pCi/L	0.4	0.5	0.3	n/a	0.4	n/a
Uranium-238	pCi/L	3.2	3.5	2.8	n/a	3.2	n/a
Thorium-228	pCi/L	2.9	3.4	2.4	n/a	2.9	n/a
Thorium-230	pCi/L	0.1	0.1	0.1	n/a	0.1	n/a
Polonium-210	pCi/L	0.9	0.9	0.9	n/a	0.9	n/a

Note: n/a: data not available; ND: not detected.

concentrations. Only motor oil range organics (180 – 310 µg/L) had a relatively high concentration, which may be caused by the heavy automobile traffic in the Carlsbad area where RW-NM samples were collected. Gasoline range organics (ND – 54 µg/L) and TICs (max: 55 µg/L) both had relatively low concentrations compared to the PW samples. There were fewer methylene blue active substances (MBAS) detected in the river water (0.04–0.12 mg/L) than in the PW samples (0.047 – 2.1 mg/L). The MBAS measurement indicates that there were anionic surfactants present in PW, which is related to the chemicals used in HF and well treatment.

Increased TDS, metal ions, radionuclides, and organics may be of concern when using Pecos River water for agriculture, industry, and municipal applications. Calcium, barium, and strontium may increase scaling, while other heavy metals and unknown organics may cause health concerns for humans and animals. High concentrations of sodium may deteriorate soil quality, and the sodium adsorption ratio (SAR) of the Pecos River water reached 11.8 (Max) in 2020; water with SAR > 9 may cause severe limitations to soil properties (Flynn, 2009). Thus, it is important to continuously monitor the Pecos River water quality and evaluate potential risks of beneficial reuse of treated PW such as surface

Table 7

Statistical results of comprehensive organic analyses of the Pecos RW-NM samples.

		Mean	Max	Min
Pesticides/Herbicides				
Endosulfan I	µg/L	0.0041	0.004	0.004
4,4'-DDD	µg/L	n/a	0.01	ND
4,4'-DDT	µg/L	n/a	0.006	ND
SVOC - PAH				
Naphthalene	µg/L	n/a	6	ND
Fluorene	µg/L	n/a	1.2	ND
SVOC - Dioxins				
2,3,7,8-TCDD	pg/L	n/a	0.14	ND
Oil and Grease				
GRO (C6-C10)	µg/L	n/a	54	ND
MRO (C20-C34)	µg/L	230	310	180
Tributyl phosphate	µg/L	3.6	5.7	1.7
Tentatively Identified Compounds (TIC)	µg/L	n/a	55	n/a

Note: n/a: data not available; ND: not detected; DDD: Dichlorodiphenyldichloroethane; DDT: Dichlorodiphenyltrichloroethane; TCDD: 2,3,7,8-Tetrachlorodibenzodioxin; PAH: Polycyclic aromatic hydrocarbon; GRO: Gasoline Range Organics; MRO: Motor oil Range Organics.

water discharge and irrigation.

4. Conclusions

This study provides the physicochemical analyses of 46 PW samples and 10 Pecos River samples from the Permian Basin in New Mexico and Texas. For PW-NM-SWD samples, 91 analytes were detected and 218 analytes were not detected (309 in total). For Pecos RW-NM samples, 67 analytes were detected and 242 analytes were not detected (309 in total). Such analyses help better understand the PW and the Pecos River water quality in the Permian Basin. The PW data can be used in selecting PW treatment and management approaches, identifying the potential for mineral recovery (e.g., ammonia, potassium, magnesium), and assisting in evaluating PW beneficial reuse feasibility and associated risks. Surface water data will be essential for establishing baseline information for potential discharge of treated PW, such as to conduct risks assessment and determine total maximum daily loading criteria for constituents of concern. Primary research findings are listed below.

- (1) PW samples from unconventional O&G operations in the Permian Basin have an average TDS of 128,423 mg/L, TOC of 103 mg/L, and ammonia of 432 mg/L. The total Ra has an average level of 469 pCi/L. Major constituents in the PW showed relatively stable temporal trends sampled between January 2020 and September 2020.
- (2) A variety of organic compounds were detected in PW-NM-SWD samples, such as VOCs, SVOCs, pesticides, organic acids, PAH, TPH, oil and grease, and unidentified compounds. The majority of the organic compounds originate from O&G development; some might be related to chemical additives, potential transformation and degradation products, and the constituents in make-up water for HF.
- (3) The Pecos RW-NM samples had more PFAS detected and at higher concentrations than the PW-NM samples, albeit 8 of 10 PFAS detected in the Pecos River and all 5 PFAS detected in the PW sample were approximations at low ng/L range (below reporting limits). This study is the first step to characterize PFAS in PW. More studies are needed to identify the temporal and spatial distribution of PFAS and the potential sources of PFAS in PW. It is also important to eliminate the PFAS cross-contamination during PW transportation, storage, sampling, analytical methodologies, or source water used for HF.
- (4) Na-Cl-Br systematics of Pecos River samples match naturally occurring shallow brine rather than unconventional PW, suggesting higher shallow brine inputs contributed to river water salinity. This interpretation is consistent with the chemical analysis results that the organic compounds detected in the Pecos River were not associated with PW origins.

CRedit authorship contribution statement

Wenbin Jiang: Methodology, Investigation, Data analysis, Writing – original draft and Writing – review & editing. **Xuesong Xu:** Methodology, Investigation, Data analysis, Writing – original draft and Editing. **Ryan Hall:** Methodology, Investigation, Data analysis, Writing – original draft and Editing, Writing – review & editing, Supervision, Funding acquisition. **Lu Lin:** Methodology, Investigation, Data analysis, Writing – original draft and Editing. **Frank Ramos:** Methodology, Investigation, Data analysis, Writing – original draft and Editing. **Mark A. Engle:**

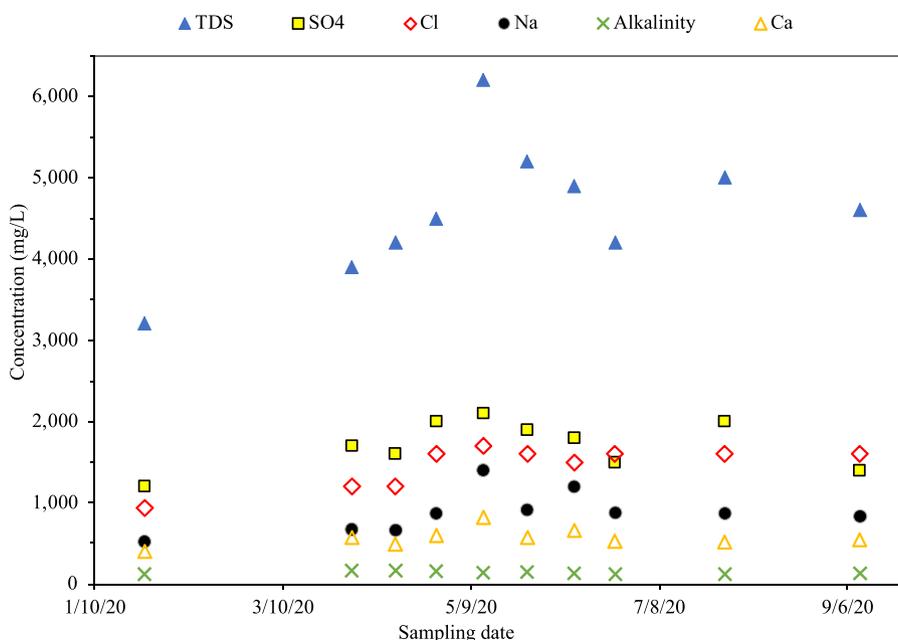


Fig. 4. Temporal change of the major constituents in ten Pecos River samples.

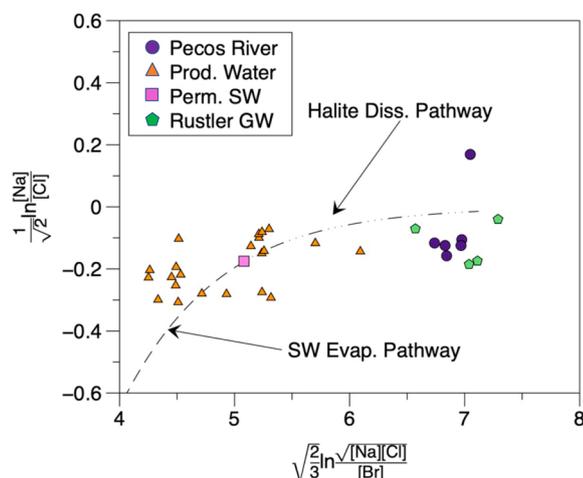


Fig. 5. Isometric log-ratio Na-Cl-Br plot showing data from Permian Basin PW, Pecos River, and Rustler aquifer groundwater samples (Siegel et al., 1991) against modeled pathways for ancient (late Permian) seawater evaporation and halite mineral dissolution. Prod. Water = produced water; Perm. SW = late Permian seawater; SW = seawater; GW = groundwater.

Methodology, Investigation, Data analysis, Writing – original draft and Editing. **Pei Xu:** Methodology, Investigation, Data analysis, Writing – original draft and Editing, Writing – review & editing, Supervision, Funding acquisition. **Yanyan Zhang:** Writing – review & editing, Supervision, Funding acquisition. **Kenneth C. Carroll:** Writing – review & editing, Supervision, Funding acquisition. **Huiyao Wang:** Writing – review & editing, Supervision, Funding acquisition. **Matthias Sayer:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data in Brief

1. Produced water quality analysis of 46 samples and statistical analysis.
2. Pecos River water quality analysis of 10 samples and statistical analysis.
3. Compounds not detected in produced water samples and Pecos River water samples.
4. Comparison with USEPA's drinking water standards.
5. Produced water sampling locations, <https://data.mendeley.com/drafts/45ptfdr37v>.

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**STATE OF NEW MEXICO
DEPARTMENT OF ENERGY, MINERALS AND NATURAL RESOURCES
OIL CONSERVATION COMMISSION**

IN THE MATTER OF PROPOSED
AMENDMENT TO THE COMMISSION'S
RULES TO ADDRESS CHEMICAL DISCLOSURE AND
THE USE OF PERFLUOROALKYL AND
POLYFLUOROALKYL SUBSTANCES AND
IN OIL AND GAS EXTRACTION,
19.15.2, 19.15.7, 19.15.14, 19.15.16 AND 19.15.25 NMAC.

Petitioner.

CASE NO. 23580

CERTIFICATE OF SERVICE

I hereby certify that on November 4, 2024, a copy of the foregoing New Energy Economy's Notice of Intent to Present the Rebuttal Technical Testimony and Exhibit of Kristen Hansen, Ph.D. of Savanna Science Consulting, the Technical Testimony itself, and Exhibit KH-4, was emailed to the persons listed below:

NM Oil Conservation Commission
Hearings:
occ.hearings@state.nm.us

Oil Conservation Commission Clerk Sheila
Apodaca:
sheila.apodaca@emnrd.nm.gov

Daniel Rubin
Assistant Attorney General
NM Dept. of Justice
408 Galisteo St.
Santa Fe, NM 87501
(505) 537-4477
drubin@nmag.gov
Attorney for New Mexico Oil Conservation

Commission

Jesse Tremaine
Chris Moander
Assistant General Counsel
New Mexico Energy Minerals and
Natural Resources Department
1220 S. St. Francis Drive
Santa Fe, NM 87505
jessek.tremaine@emnrd.nm.gov
chris.moander@emnrd.nm.gov
*Attorneys for New Mexico Oil Conservation
Division*

Nicholas Maxwell
P.O. Box 1064
Hobbs, New Mexico 88241
(575) 441-3560
inspector@sunshineaudit.com

Michael H. Feldewert
Adam G. Rankin
Julia Broggi
Paula M. Vance
Holland & Hart, LLP
Post Office Box 2208
Santa Fe, New Mexico 87504
(505) 988-4421
mfeldewert@hollandhart.com
agrarkin@hollandhart.com
jbroggi@hollandhart.com
pmvance@hollandhart.com
camulcahy@hollandhart.com
Attorneys for NMOGA

Deana M. Bennett
Chandler R. Farnworth
Jordan L. Kessler
Modrall, Sperling, Roehl, Harris & Sisk,
P.A.
Post Office Box 2168
500 Fourth Street NW, Suite 1000
Albuquerque, New Mexico 87103-2168
(505) 848-1800
Deana.bennett@modrall.com
cfarnworth@modrall.com
Jordan_Kessler@EOGResources.com
Attorneys for EOG Resources, Inc.

Tim Davis
Samantha Ruscavage_Barz
WildEarth Guardians
301 N. Guadalupe St., Ste. 201
Santa Fe, New Mexico 87501
(205) 913-6425
tdavis@wildearthguardians.org
sruscavagebarz@wildearthguardians.org
Attorney for WildEarth Guardians

Respectfully,

/s/ Mariel Nanasi

Mariel Nanasi, Esq.

Attorney for New Energy Economy

300 East Marcy St.

Santa Fe, NM 87501

(505) 469-4060

mariel@seedsbeneaththesnow.com