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Solid-phase extraction followed by gas chromatography-mass spectrometry for the quantitative analysis of semi-volatile hydrocarbons in hydraulic fracturing wastewaters

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A versatile method was developed for the quantitative analysis of semi-volatile linear aliphatic hydrocarbons in the *n*-C_{10} to *n*-C_{32} range and 16 polycyclic aromatic hydrocarbons (PAH) in hydraulic fracturing wastewaters using solid-phase extraction (SPE) on disposable octadecyl-bonded silica (C_{18}) cartridges followed by gas chromatography-mass spectrometry. Matrix spikes revealed SPE recovery rates in the range of 38–120% for linear aliphatic hydrocarbons (*n*-C_{10} to *n*-C_{32}) and 84–116% for PAH. Limits of detection were in the lower ng L^{-1} range for both compound groups. To prove the practicability of the developed method in real applications, the treatment performance of a hybrid forward osmosis–reverse osmosis pilot system treating produced water from the Denver-Julesburg basin in Colorado was assessed over a period of eight weeks. The removal efficiency of the overall system after reverse osmosis treatment for *n*-alkanes was constantly better than 99.4%. The lower molecular weight PAH naphthalene, fluorene, and phenanthrene were the most abundant PAH detected in the produced water feed, filtrate and concentrate streams during treatment. Their concentrations in the produced water feed reached up to 359.3 μg L^{-1}, 40.7 μg L^{-1}, and 68.3 μg L^{-1}, respectively. However, naphthalene (0.5 ± 0.2 μg L^{-1}) was the only analyzed PAH in the final treated water that exceeded the general US Environmental Protection Agency maximum contaminant level for PAH in drinking water of 0.2 μg L^{-1}.

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1. Introduction

Recently, several publications targeting analytical approaches for produced water and hydraulic fracturing flowback from unconventional oil and gas (O&G) production expressed the immediate need for robust analytical methods for the quantification of (trace) organic chemicals in hydraulic fracturing waters.[1,2] In simplified terms, hydraulic fracturing waters are mainly composed of two types of contaminants: (1) compounds that are native in geologic shale formations and naturally occurring water therein, and (2) chemicals that are present in the fracking fluids used to fracture the formation and stimulate the wells. Therefore, contaminant fraction and composition is highly dependent on natural (*i.e.*, geologic formation) and anthropogenic (*i.e.*, chemical composition of fracking fluids) factors and is likely to vary geographically and over time depending on which water type (flowback, produced water) is recovered from the fractured well.[1] However, it also depends on how long the fractured well is shut in before flowing back, which can be up to several months. Produced water is mainly composed of formation water and is generally saturated with natural compounds such as hydrocarbons (*e.g.*, polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons), inorganics (*e.g.*, salts), and naturally occurring radioactive material that can originate from the formation rock, and the free or emulsified O&G trapped in the formation.

Despite potential environmental and human health risks originating from unconventional O&G production, organic compounds in hydraulic fracturing wastewaters have not been widely characterized yet. Hydrocarbons are probably the class of compounds that has been studied in greatest detail. Hydrocarbons can occur in hydraulic fracturing wastewaters in various forms: dissolved, associated with non-aqueous phase liquids, associated with colloids, and adsorbed or incorporated into particles. Water solubility of hydrocarbons in water is mostly dependent upon temperature, pH, ionic strength (concentration of soluble salts), and other organic components present in the water phase. Water solubility generally tends to decrease as the number of carbons in the chain of linear aliphatic hydrocarbons increase. Furthermore, aliphatic hydrocarbons tend to be less soluble in water than aromatic hydrocarbons of similar molecular weight; hence, low molecular weight hydrocarbons are found predominantly in the dissolved phase and high molecular weight hydrocarbons in the particulate phase.[3] Despite their

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comparatively low water solubility (ranging from 31 mg L^{-1} for naphthalene to 0.3 μg L^{-1} for benzo(ghi)perylene at 25 °C), both European Union and US Environmental Protection Agency (EPA) listed 16 PAH pollutants for priority monitoring in water and wastewater (Directive 76/464/EEC and its daughter directives) based on their highly hazardous nature.

So far, studies about the quantitative analysis of individual semi-volatile organic compounds in hydraulic fracturing waters are scarce.[4,5] One of the reasons is that sample pretreatment and pre-concentrating pose certain difficulties for analysis of organic constituents due to the variable nature of water samples and the wide range of hydrochemical parameters (*i.e.*, total organic carbon, turbidity, salinity, pH). A detailed review of analytical approaches for the analysis of chemical constituents in hydraulic fracturing waters is provided by Ferrer and Thurman.[1] With the increasing need for water reuse, reliable quantitative analytical methods are needed for organic indicator compounds such as PAH over a wide range of water types (*i.e.*, source water, filtrate and concentrate streams during treatment, final treated water) to assess the performance of advanced processes (*e.g.*, reverse osmosis (RO) and nanofiltration) for treatment of O&G wastewaters. Because solid phase extraction (SPE) has been used as a pre-concentrating method for analysis of PAH in waters with high salinity[6] and high concentrations of suspended solids,[7] it can potentially be employed for the analysis of aromatic and aliphatic hydrocarbons in hydraulic fracturing waters. In general, SPE techniques allow a better characterization of water samples with complex matrices by pre-concentrating trace components present in the sample and by excluding inorganic components (*i.e.*, high salinity) and insoluble particles that can interfere with liquid chromatography (LC) or gas chromatography (GC) coupled with mass spectrometry (MS). To our knowledge, SPE has only been used so far for sample pretreatment during the analysis of cocamide diethanolamines in hydraulic fracturing waters by LC coupled with high-resolution-MS.[5]

Here, we present a versatile method for the quantitative analysis of semi-volatile linear aliphatic hydrocarbons in the *n*-C_{10} to *n*-C_{32} range and 16 PAH in hydraulic fracturing waters using SPE on disposable octadecyl-bonded silica (C_{18}) cartridges followed by GC-MS. A total of 27 samples of O&G wastewater, treated by a pilot-scale forward osmosis–reverse osmosis (FO–RO) hybrid treatment system, were analyzed over a period of eight weeks in spring 2015 to provide a proof-of-concept that the developed method is suitable for the quantitative assessment of O&G wastewater treatment performance.

2. Material and methods

2.1. Chemicals

All organic solvents (*n*-hexane, acetone, methylene chloride, 2-propanol, methanol) and ultrapure water were of HPLC grade and obtained from Sigma Aldrich (St. Louis, MO). *p*-Terphenyl-d_{14} and PAH calibration mix (10 μg mL^{-1} each in acetonitrile) containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenz(*a*,*h*)anthracene, benzo(ghi)perylene, and indeno(1,2,3-*c*,*d*)pyrene were purchased from Supelco (Bellefonte, PA). 2-Fluorobiphenyl and 1,1′-binaphthyl were obtained from Acros Organics (Fisher Scientific, Pittsburgh, PA). *n*-Alkanes calibration mix (all even, *n*-C_{10} to *n*-C_{40}, 50 μg mL^{-1} each in *n*-heptane) and tetracosane-d_{50} were purchased from Sigma Aldrich. Stock solutions (1 μg μL^{-1}) of 1,1′-binaphthyl, 2-fluorobiphenyl, and *p*-terphenyl-d_{14} were prepared in methylene chloride, while tetracosane-d_{50} stock solution (1 μg μL^{-1}) was prepared in *n*-hexane. All stock solutions were stored at 5 °C, tightly capped and wrapped with lab wrapping film in order to avoid any evaporation. Working standard solutions of PAH and *n*-alkanes were obtained by appropriate dilution of stock solutions.

2.2. Automated solid phase extraction conditions

Samples were pretreated using an AutoTrace 280 SPE unit (Thermo Scientific, Waltham, MA). Application Brief 876,[8] which is geared towards an automated solution of US EPA Method 625, was used as a basis for developing the current automated SPE procedure. SPE was performed using 6 mL Thermo Scientific Dionex SolEx C_{18} cartridges (0.5 g adsorbate). Because the AutoTrace 280 allows extraction of samples with high amounts of suspended solids, samples were not filtered prior to analysis to avoid the loss of analytes that were not truly dissolved or would have sorbed to the filter material. However, a fraction of one produced water sample was filtered with a 0.45 μm PTFE membrane filter (Pall, Port Washington, NY) and was used for matrix spiking experiments. Hence, highly concentrated samples with dissolved organic carbon (DOC) of more than 100 mg L^{-1} were diluted with ultrapure water at a ratio of 1 : 10 or 1 : 100 to a total volume of 100 mL, respectively to prevent SPE cartridges from clogging and analyte breakthrough. Less organic rich samples (*i.e.*, post FO–RO membrane treatment) required further enrichment, resulting in sample volumes of up to 400 mL. Accordingly, enrichment factors during SPE ranged from 2 to 800, depending on the sample type. To keep the more hydrophobic analytes in solution, 10% of 2-propanol (v/v) was added to each water sample as a modifier.[9] Two surrogate standards suggested by US EPA Method 625, 2-fluorobiphenyl and *p*-terphenyl-d_{14}, were spiked into each water sample (5 μL of 1 μg μL^{-1} standard) prior to SPE to assess extraction performance and potential matrix interferences. Samples were not adjusted in terms of pH and salt concentration. As detailed in Section 3.2, the pH of samples was between 6 and 7, whereas salt concentration (except for ultrapure water samples) was generally between 0.3 g L^{-1} and 50 g L^{-1}. Due to the high hydrophobicity of most hydrocarbon compounds (log K_{ow} ranging from 3.4 for naphthalene to >7.04 for benzo(ghi)perylene), a mixture of *n*-hexane/acetone was chosen as the elution solvent. Cartridges were conditioned with 3 mL *n*-hexane/acetone 1 : 1 (v/v), 3 mL of methanol, followed by 5 mL of ultrapure water. The water samples (100–400 mL) were passed through each cartridge with a flow of 4 mL min^{-1}. The sample loading volume was set 40% above the actual volume to prevent incomplete loading of sample on the SPE cartridge. The cartridges were rinsed with 5 mL of ultrapure water after sample

loading was completed and were immediately dried under a nitrogen stream for 1 hour. Analytes were eluted three times from the cartridges with 3 mL of *n*-hexane/acetone 1 : 1 (v/v) each at a flow rate of 2 mL min^{-1}. The eluate was combined in graduated vials and evaporated under a gentle nitrogen stream at room temperature (20 °C) to a final volume of 500 μL using a N-EVAP112 nitrogen evaporation unit (Organomation Associates, Inc., Berlin, MA). Complete dryness of sample eluates was strictly avoided to prevent losses of more volatile compounds. Subsequently, eluates (500 μL) were transferred into 1.5 mL amber glass GC vials. 1,1′-Binaphthyl (2 μL of 1 μg μL^{-1} standard) and *n*-tetracosane-d_{50} (4 μL of 1 μg μL^{-1} standard) were added to each sample as internal quantification standards for immediate GC-MS analysis. After each SPE run, the AutoTrace 280 sample loading channels and Teflon tubing were rinsed with acetone followed by ultrapure water to prevent carry-over of analytes. All of the used glassware was thoroughly cleaned with Alcanox detergent followed by methanol rinse and oven drying.

2.3. Gas chromatography-mass spectrometry

Samples were analyzed by a HP 6890 gas chromatograph equipped with a HP 5973 single quadrupole mass spectrometer from Agilent Technologies (Palo Alto, CA) using a Rtx-5Sil MS capillary column (30 m length, 0.25 mm internal diameter, 0.25 μm film thickness; Restek, Bellefonte, PA) and the following oven temperature program: 60 °C (held for 2 min), then increased at 9 °C min^{-1} to 300 °C (held for 15 min). Ultra high purity helium was used as carrier gas at a constant flow rate of 1 mL min^{-1}. Sample injections (2 μL) were made in splitless mode using an Agilent 7683 series autosampler. Injector temperature was set at 245 °C. The GC-MS transfer line temperature was maintained at 280 °C and the ion source temperature was held at 220 °C. The mass spectrometer was operated in electron ionization mode (70 eV). Mass spectra were recorded in full scan mode (*m*/*z* 50–600). Solvent delay was set at 5 min. ChemStation software (Agilent, version B.04.01) was used to process the acquired data. All mass spectra were compared with spectra in the Wiley AccessPak spectral library, 8th edition (Palisade, Ithaca, NY).

2.4. Identification and quantification of analytes

Identification of analytes was achieved by mass spectra (Wiley AccessPak spectral library) and retention times of analytical standards. Analytes were quantified by internal standard method.[10] The isotopic labeled internal standard tetracosane-d_{50} was used for the quantification of linear aliphatic hydrocarbons (*n*-C_{10} to *n*-C_{32}) in full scan mode whereas 1,1′-binaphthyl was used as internal standard for the quantification of PAH in selected ion monitoring (SIM) mode.[11]

In brief, analyte concentrations in water samples were calculated by measuring the peak areas of each compound relative to the peak area of the respective internal standard. The ratio between the peak area of an analyte and the peak area of the internal standard (both measured in total ion chromatogram TIC) is described as response factor *R*. As a rule of thumb, the *R* factor is close to 1 for compounds with similar structure and mass fragmentation pattern. Thus, an *R* factor of 1 was applied for all aliphatic hydrocarbons that were analyzed in TIC to allow quantification of compounds whereof no calibration standards were available (*e.g.*, odd *n*-C_{11}–*n*-C_{31}).

Due to the significantly lower abundance of PAH in the water samples and potential co-elution of compounds, quantification of these analytes was performed in SIM mode. Therefore, another correction factor *K* was necessary to specify the relation between the peak area of a compound in the TIC and its peak area in the mass trace. To determine the analyte specific *R*- and *K*-factors, PAH calibration standards, including internal standard 1,1′-binaphthyl, were injected into the GC-MS system at the beginning and end of each sample sequence. The resulting peak areas of the 16 PAH were compared with the peak area of the internal standard 1,1′-binaphthyl. Correction (*K*) and response (*R*) factors for the 16 PAH were estimated according to eqn (1) and (2):

$$K = \frac{A_{\mathrm{TIC}}}{A_{m/z}} \tag{1}$$

$$R = \frac{A_{\mathrm{TIC}}}{m_{\mathrm{A}}} \frac{m_{\mathrm{IS}}}{A_{\mathrm{IS}}} \tag{2}$$

where A_{TIC} is the peak area of the analyte in TIC, $A_{m/z}$ is the peak area of the analyte in mass trace *m*/*z*, A_{IS} is the peak area of the internal standard in TIC, m_{A} is the mass of the analyte, and m_{IS} is the mass of the internal standard. Ions used for quantification in SIM mode are summarized in Table 1. On the basis of these *R*- and *K*-factors, analyte concentrations (C_{A}) in water samples were calculated according to eqn (3):

$$C_{\mathrm{A}} = \frac{A_{m/z}}{A_{\mathrm{IS}}} \frac{m_{\mathrm{IS}}}{V_{\mathrm{sample}}} \frac{1}{R} K \tag{3}$$

where V_{sample} is the volume of the water sample.

2.5. Pilot-scale FO–RO hybrid system

Water samples were collected from a pilot-scale FO–RO hybrid treatment system used to dewater produced water from O&G operations in the Denver-Julesburg basin, Colorado (Fig. 1). Similar pilot-scale treatment system configurations have been previously described by Hancock *et al.*,[12] Coday *et al.*,[13] and Holloway *et al.*[14] In FO, a concentrated draw solution induces an osmotic pressure difference across a semipermeable membrane to extract water from impaired streams, thereby concentrating it and reducing residual management costs.[15] Three 4040 spiral wound cellulose triacetate (CTA) membrane elements (Hydration Technology Innovations (HTI), Albany, OR) with approximately 6.3 m^2 total membrane area were employed; the membrane elements were manufactured with corrugated chevron feed spacers and triple layer tricot spacers in the draw solution channel.[16] During operation raw produced water was circulated through the feed channel of the membrane elements at 82 L min^{-1}, while a sodium chloride (NaCl) brine (55 g L^{-1}) was recirculated through the draw solution channels at 1.5 L min^{-1}. Diluted NaCl brine from the FO system was continually reconcentrated by a downstream RO pilot-scale system and returned to the FO system. The

Table 1 Analytical parameters for 16 priority PAH analyzed by C_{18} SPE followed by GC-MS. Surrogate standards (SS) were used according to US EPA Method 625[c]

Compound	Formula	MW [g mol^{-1}]	R_t [min]	Quantifier ion[a] [m/z]	MDL [ng L^{-1}]	MQL [ng L^{-1}]	K-Factor[b]	R-Factor[b]
Naphthalene	$C_{10}H_8$	128.2	9.39	128 (102)	12	40	1.96	0.48
2-Fluorobiphenyl (SS)	$C_{12}H_9F$	172.2	12.22	172 (85)	8	27	2.81	0.39
Acenaphthylene	$C_{12}H_8$	152.2	13.50	152 (150)	6	19	1.31	0.62
Acenaphthene	$C_{12}H_{10}$	154.1	13.97	154 (152)	8	28	3.54	0.69
Fluorene	$C_{13}H_{10}$	166.2	15.35	166 (163)	4	13	3.14	0.72
Phenanthrene	$C_{14}H_{10}$	178.2	17.86	178 (176)	9	28	2.34	0.91
Anthracene	$C_{14}H_{10}$	178.2	17.99	178 (176)	8	26	2.29	0.85
Fluoranthene	$C_{16}H_{10}$	202.3	21.00	202 (200)	10	33	2.31	0.91
Pyrene	$C_{16}H_{10}$	202.3	21.57	202 (200)	7	23	2.34	0.93
p-Terphenyl-d_{14} (SS)	$C_{18}D_{14}$	244.4	22.18	244 (122)	9	29	2.85	0.58
Benz(*a*)anthracene	$C_{18}H_{12}$	228.3	24.78	228 (226)	10	32	2.70	0.80
Chrysene	$C_{18}H_{12}$	228.3	24.87	228 (226)	10	33	2.70	0.90
Benzo(*b*)fluoranthene	$C_{20}H_{12}$	252.3	27.44	252 (250)	12	39	2.70	0.77
Benzo(*k*)fluoranthene	$C_{20}H_{12}$	252.3	27.51	252 (250)	11	37	2.84	0.90
Benzo(*a*)pyrene	$C_{20}H_{12}$	252.3	28.17	252 (250)	7	22	2.93	0.77
Indeno(1,2,3-*c*,*d*)pyrene	$C_{22}H_{12}$	276.3	30.79	276 (274)	9	29	3.39	0.70
Dibenz(*a*,*h*)anthracene	$C_{22}H_{14}$	278.4	30.90	278 (276)	13	42	3.80	0.82
Benzo(ghi)perylene	$C_{22}H_{12}$	276.3	31.50	276 (274)	8	28	3.54	0.81

[a] Confirmation ion provided in parenthesis. [b] Response (R) and correction (K) factors were determined for each GC-MS sample sequence. [c] Abbreviations: MW – molecular weight; R_t – retention time; MDL – method detection limit; MQL – method quantification limit; SS – surrogate standard.

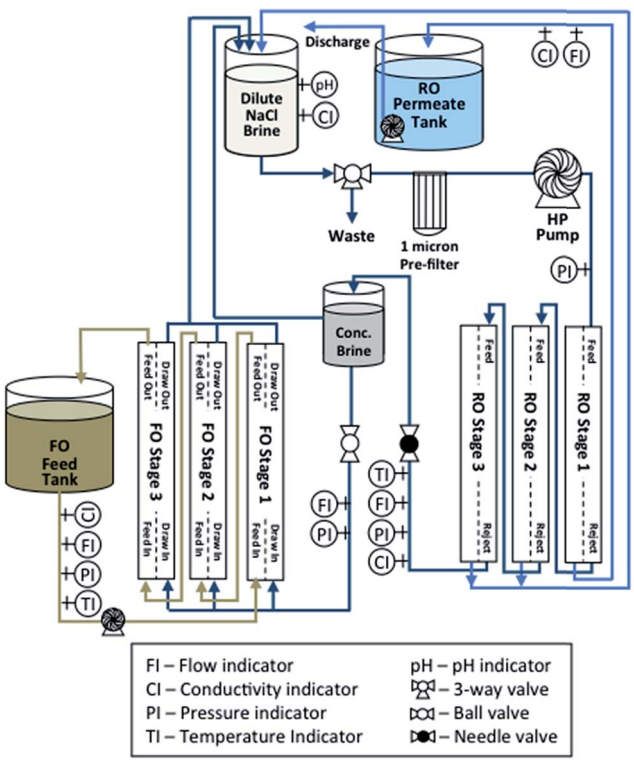

Fig. 1 Simplified process flow diagram of the pilot-scale FO–RO hybrid treatment system (adapted from Hancock *et al.*).[12]

RO system employed three SW30-2540 spiral wound polyamide thin-film composite (TFC) membranes from Dow Filmtec (Edina, MN) and operated at 980 psi with a feed flow rate of 5.7 L min^{-1}.

Each experiment was conducted in batch mode, where 900 L of produced water feed solution and 40 L of NaCl draw solution were recirculated in the FO system for 24 h. During each 24 h period, the FO system would recover approximately 550 L from the produced water and concentrate the solution by 2.3 times. At the end of the 24 h period, the remaining 350 L of concentrated produced water was drained from the system, replaced with fresh produced water, and the run was repeated; the NaCl draw solution was not replaced between each run. This procedure was repeated 3–4 times for each experiment before the systems were taken offline for cleaning. It should be noted that the FO and RO membranes are semipermeable and therefore typically exhibit high rejection (>95–99.7%) of dissolved inorganic and organic contaminants.

Three samples were collected for analysis after the first hour of operation and every 24 hours thereafter. One 250 mL sample was collected from the produced water feed solution prior to entering the FO system. One 500 mL sample each were collected from the NaCl draw solution and from the permeate stream of the RO system. Amber glass sample bottles were rinsed with acetone prior to sampling to prevent sample contamination. Samples were stored without headspace at 5 °C until preparation and analysis to minimize losses due to volatilization and biodegradation.

3. Results and discussion

3.1. Automated solid phase extraction performance

3.1.1. Polycyclic aromatic hydrocarbons. Linearity, recovery, repeatability, method detection limit (MDL), and method quantification limit (MQL) were evaluated for each PAH (Tables 1 and 2) using C_{18} SPE cartridges under the previously described

extraction conditions. For determination of recovery efficiencies, water samples were spiked with a defined amount of analyte prior to SPE as summarized in Table 2. Each matrix spiking experiment was carried out in quadruplicate. External six-point calibration curves (in triplicate) were prepared in ultrapure water for each compound in the PAH calibration standard as well as the two surrogate standards with concentrations between 10 and 1000 ng mL^{-1} in the final extract. The linearity was calculated using the relationship between areas and concentrations of compounds with excellent correlation coefficients exceeding 0.995.

For most PAH, the recoveries in spiked ultrapure water samples ranged from 71 to 127%, except for naphthalene (141%), dibenz(*a*,*h*)anthracene (30%), and benzo(ghi)perylene (38%). The lower recovery of the last two compounds was due to their higher molecular weight and stronger hydrophobicity (*i.e.*, less water soluble, sorptive losses), whereas the higher recovery of the first resulted potentially from contamination. Procedural blanks and control samples were performed on a regular basis and blanks for the C_{18} cartridges contained some trace levels of the low molecular weight PAH naphthalene. Interestingly, recoveries of PAH in spiked matrix samples ($n = 4$) were significantly enhanced and were in the range of 85–112% for draw solution, 84–107% for RO permeate, and 84–116% for produced water (1 : 10 v/v diluted with ultrapure water), respectively (Table 2). Besides naphthalene, fluorene, and phenanthrene, for which recoveries were corrected, none of the other PAH were present in the background of the used draw solution and RO permeate samples, respectively. In the spiked produced water samples recoveries of naphthalene, fluorene, phenanthrene, pyrene, benz(*a*)anthracene, chrysene, and benzo(*a*)pyrene were corrected by their respective background values. The higher ionic strength in the matrix samples seemed to increase SPE efficiency for PAH with higher molecular weight. The relative standard deviations (RSD) between recovery efficiencies calculated for replicated samples were in general below 20% and overall satisfactory for most of the analyzed compounds (Table 2). Slightly better RSD were observed in spiked matrix samples compared to spiked ultrapure water samples. Rather poor performance was achieved for both surrogate standards. Though consistent (and expected due to its hydrophobicity), recoveries of *p*-terphenyl-d_{14} in spiked ultrapure water, draw solution, and RO permeate were only 13%, 16%, and 6% with RSD of 30%, 25%, and 57%, respectively. Performance of 2-fluorobiphenyl was clearly dependent on the sample matrix, which resulted in 95 ± 29% recovery in spiked ultrapure water but only 25 ± 10% and 17 ± 10% recovery in spiked draw solution and RO permeate, respectively. We hypothesize that the high ionic strength of the draw solution favored volatilization of 2-fluorobiphenyl during SPE. With these findings we refrained from correcting target analyte peak areas for potential analyte losses during SPE based on surrogate standard peak areas, but note that additional work is necessary to find more appropriate surrogate standards for the analysis of hydraulic fracturing wastewaters using SPE. Furthermore, spiking procedures of hydrophobic surrogate standards into

Table 2 Recovery efficiencies for 16 priority PAH in spiked matrix samples analyzed by C_{18} SPE followed by GC-MS. Number of sample replicates (*n*) is provided for each water type[c]

	0.4 μg spiked in 100 mL ultrapure water ($n = 4$)		0.4 μg spiked in 100 mL draw solution ($n = 4$)		0.4 μg spiked in 100 mL RO permeate ($n = 4$)		0.4 μg spiked in 100 mL produced water ($n = 3$)[a]		0.4 μg spiked in 100 mL produced water ($n = 3$)[b]	
Compound	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]
Naphthalene	140.9	3.0	111.8	1.8	107.2	2.6	95.5	4.2	92.5	9.1
2-Fluorobiphenyl (SS)	94.7	29.0	25.3	12.4	17.4	9.8	N/A	N/A	N/A	N/A
Acenaphthylene	115.3	17.9	110.5	3.8	83.8	1.4	84.2	2.8	74.8	16.9
Acenaphthene	127.0	13.5	114.9	1.0	90.5	2.3	116.3	2.1	88.7	14.2
Fluorene	115.8	13.1	115.7	4.7	90.8	1.1	86.0	0.4	87.7	1.4
Phenanthrene	98.2	16.7	93.7	11.2	93.1	3.1	83.4	1.2	91.8	2.3
Anthracene	95.2	19.2	104.1	6.3	91.9	7.6	100.9	2.4	88.0	6.0
Fluoranthene	70.7	18.0	104.1	5.3	98.0	3.8	87.0	1.0	96.1	9.7
Pyrene	70.9	18.5	98.8	4.2	93.9	3.6	89.3	1.2	93.7	12.4
p-Terphenyl-d_{14} (SS)	12.9	30.2	16.3	25.4	5.7	52.7	N/A	N/A	N/A	N/A
Benz(*a*)anthracene	79.4	22.6	95.9	10.4	97.4	4.7	89.0	1.2	91.8	6.5
Chrysene	71.8	16.3	84.9	12.3	93.2	5.0	95.1	0.1	95.9	6.4
Benzo(*b*)fluoranthene	83.7	14.8	97.6	15.1	93.5	6.3	91.5	7.0	89.4	7.8
Benzo(*k*)fluoranthene	81.1	9.1	87.2	15.3	91.2	7.1	84.2	2.9	87.5	5.2
Benzo(*a*)pyrene	86.9	10.3	86.8	13.0	86.3	6.6	88.0	5.1	92.9	9.6
Indeno(1,2,3-*c*,*d*)pyrene	73.3	5.2	98.7	14.7	88.5	9.2	95.2	4.7	94.5	9.8
Dibenz(*a*,*h*)anthracene	29.8	9.6	96.7	11.1	97.5	9.2	97.6	6.4	90.1	11.7
Benzo(ghi)perylene	38.4	16.5	92.3	10.2	92.1	9.7	95.9	8.8	95.7	11.2

[a] 0.45 μm PTFE membrane filtered produced water diluted with ultrapure water at a ratio of 1 : 10 (v/v). Spiking occurred after filtration. [b] Unfiltered produced water diluted with ultrapure water at a ratio of 1 : 10 (v/v). [c] Abbreviations: N/A – data not available; RO – reverse osmosis; RSD – relative standard deviation; SS – surrogate standard.

water samples could be improved by using more water-miscible solvents (*e.g.*, acetone).

For analytes that were not present in procedural blanks, the MDL and the MQL for each compound in ultrapure water were calculated from the signal to noise ratio of each individual peak. The MDL was defined as the lowest concentration that gave a signal to noise ratio that was greater than 3. The MQL was defined as the lowest concentration that gave a signal to noise ratio that was greater than 10. For analytes present in procedural blanks (*i.e.*, naphthalene), MDL was calculated as three times the standard deviation of the respective analyte in the blanks. The MDL and MQL ranged from 4 to 13 ng L^{-1} and from 13 to 42 ng L^{-1}, respectively. These limits are similar to other studies that used off-line SPE for determination of PAH in aqueous samples.[9] The use of C_{18} cartridges for SPE efficiently and reliably removed constituents from the water samples (*e.g.*, inorganic ions) that might have caused interferences with the GC-MS measurements.

3.1.2. Linear aliphatic hydrocarbons. The extraction efficiency of 12 even *n*-alkanes spiked into draw solution (5 μg each into 100 mL), RO permeate (0.8 μg each into 100 mL), and produced water (0.8 μg each into 100 mL, 1 : 10 v/v diluted with ultrapure water) ranged between 40 and 120%, 38 and 84%, and 59 and 90%, respectively (Table 3). Each matrix spiking experiment was carried out in triplicate and recoveries were corrected for background concentrations of *n*-alkanes. The lowest recovery values were found for the long-chain *n*-alkanes (*n*-C_{30} and *n*-C_{32}), which is most likely related to their higher molecular weight and lower water solubility. *n*-Alkanes with higher molecular weight than *n*-C_{32} were not targeted in this study. RSD were comparable with those obtained for PAH. Recovery rates determined from *n*-alkanes directly loaded on top of C_{18} cartridges during SPE (instead of being spiked into the water sample) were in the range of 96–122% with RSD below 10% and emphasize the general suitability of C_{18} cartridges for extraction of dissolved hydrocarbons from aqueous samples (Table 3). Calibration curves (10 to 1000 ng mL^{-1}) were generated for 12 even *n*-alkanes (*n*-C_{10}–*n*-C_{32}) as described for PAH in Section 3.1.1, and the calculated linearity exceeded 0.994. As expected, calculated relative response factors indicated a similar GC-MS response of *n*-alkanes and the internal standard tetracosane-d_{50} (*R* factor of 1.1 for *n*-C_{10} and 1.0 for *n*-C_{32}), validating the approach of using a general response factor of 1 for the quantification of linear aliphatic hydrocarbons in TIC. The MDL and MQL ranged from 34 to 167 ng L^{-1} and from 118 to 567 ng L^{-1}, respectively (Table 4). None of the analyzed even *n*-alkanes were detected in procedural blanks.

Table 4 Analytical parameters for twelve even linear aliphatic hydrocarbons analyzed by C_{18} SPE followed by GC-MS[a]

Compound	Formula	MW [g mol^{-1}]	R_t [min]	MDL [μg L^{-1}]	MQL [μg L^{-1}]
n-C_{10}	$C_{10}H_{22}$	142	6.06	0.057	0.191
n-C_{12}	$C_{12}H_{26}$	170	9.55	0.087	0.288
n-C_{14}	$C_{14}H_{30}$	198	12.69	0.118	0.396
n-C_{16}	$C_{16}H_{34}$	226	15.49	0.137	0.465
n-C_{18}	$C_{18}H_{38}$	254	17.99	0.154	0.535
n-C_{20}	$C_{20}H_{42}$	282	20.24	0.088	0.293
n-C_{22}	$C_{22}H_{46}$	310	22.29	0.046	0.158
n-C_{24}	$C_{24}H_{50}$	338	24.18	0.034	0.118
n-C_{26}	$C_{26}H_{54}$	366	25.92	0.047	0.159
n-C_{28}	$C_{28}H_{58}$	394	27.55	0.081	0.27
n-C_{30}	$C_{30}H_{62}$	422	29.09	0.167	0.567
n-C_{32}	$C_{32}H_{66}$	450	30.78	0.144	0.484

[a] Abbreviations: MW – molecular weight; R_t – retention time; MDL – method detection limit; MQL – method quantification limit.

Table 3 Recovery efficiencies for twelve even linear aliphatic hydrocarbons in spiked matrix samples analyzed by C_{18} SPE followed by GC-MS. Number of sample replicates (*n*) is provided for each water type[b]

	1 μg spiked directly on SPE cartridge ($n = 3$)		5 μg spiked in 100 mL draw solution ($n = 3$)		0.8 μg spiked in 100 mL RO permeate ($n = 3$)		0.8 μg spiked in 100 mL produced water ($n = 3$)[a]	
Compound	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]
n-C_{10}	95.8	4.1	119.5	16.1	N/A	N/A	N/A	N/A
n-C_{12}	99.4	3.1	91.7	9.7	84.0	12.4	75.7	9.7
n-C_{14}	108.8	3.6	75.8	16.6	69.5	3.7	67.3	12.4
n-C_{16}	122.3	9.4	65.8	15.3	62.9	0.4	81.8	5.0
n-C_{18}	116.5	9.7	57.6	17.2	76.6	4.4	76.0	2.1
n-C_{20}	118.5	1.4	63.9	11.6	74.4	11.4	89.7	4.0
n-C_{22}	112.1	5.6	50.3	19.9	63.2	15.6	73.3	21.0
n-C_{24}	108.7	0.2	49.6	20.3	71.5	3.4	68.3	15.2
n-C_{26}	101.0	2.0	54.6	19.7	61.8	7.8	66.6	15.2
n-C_{28}	107.2	1.2	53.6	15.7	62.2	14.8	73.3	10.8
n-C_{30}	101.8	2.0	44.7	13.5	45.3	3.1	69.5	19.2
n-C_{32}	99.6	2.7	39.6	8.4	37.7	14.6	59.2	13.3

[a] 0.45 μm PTFE membrane filtered produced water diluted with ultrapure water at a ratio of 1 : 10 (v/v). Spiking occurred after filtration. [b] Abbreviations: N/A – data not available; RO – reverse osmosis; RSD – relative standard deviation.

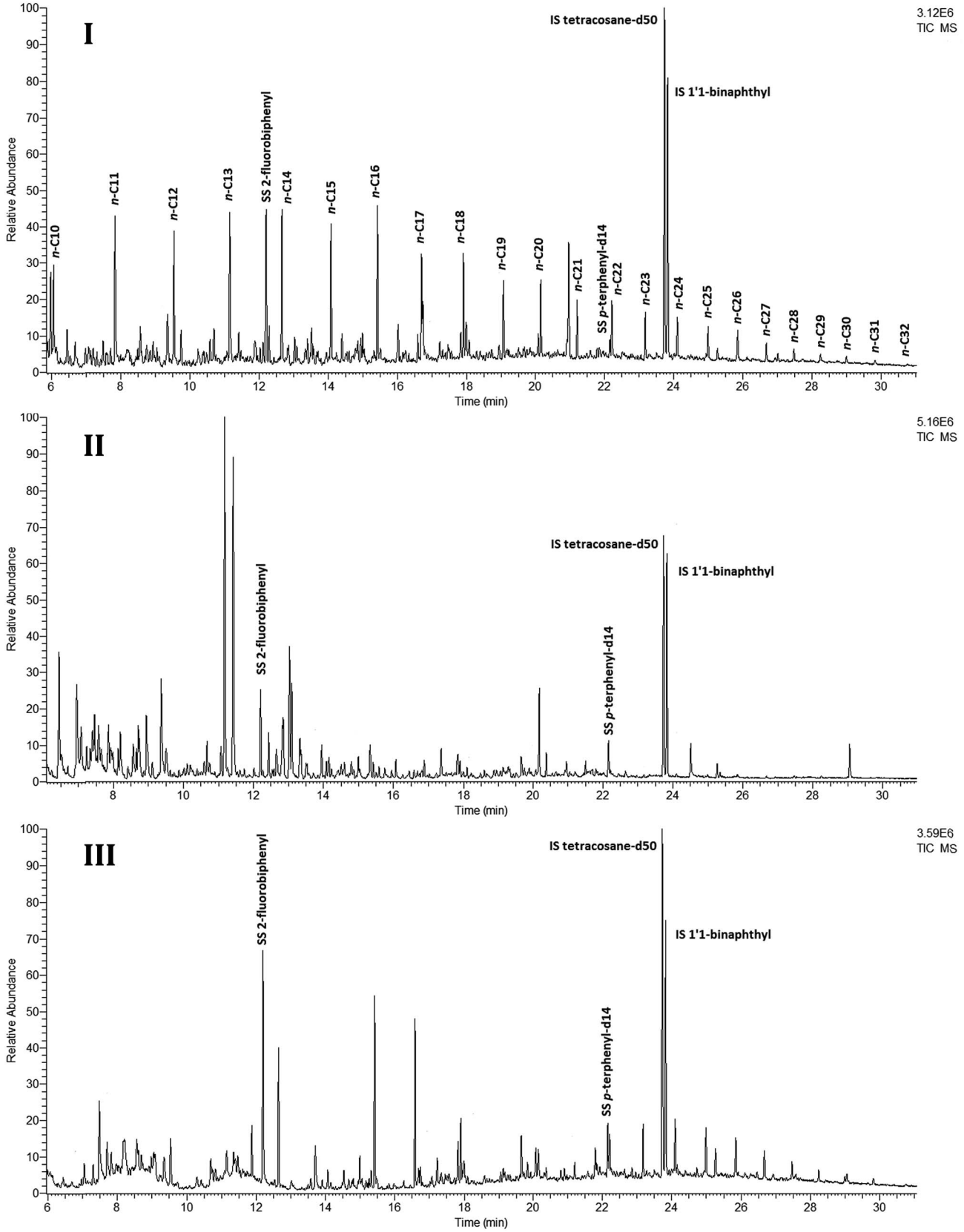

Fig. 2 Total ion chromatograms (TIC) of (I) produced water (1 mL sample enriched during solid phase extraction), (II) draw solution (400 mL sample enriched), and (III) RO permeate (400 mL sample enriched). Note that draw solution and RO permeate TIC are 400-times magnified compared to the produced water TIC. IS – internal standard, SS – surrogate standard.

3.2. Analysis of selected compounds in hydraulic fracturing wastewaters

To prove the practicability of the developed method in real applications, treatment performance of a hybrid FO–RO pilot system treating produced water from the Denver-Julesburg basin in Colorado was assessed over a period of eight weeks in spring 2015. Nine produced water samples as well as 18 corresponding draw solution and RO permeate samples were analyzed and target aromatic and aliphatic hydrocarbons quantified. In general, the DOC and TSS concentrations of the raw produced water were 300 mg L^{-1} and 80 mg L^{-1}, respectively. The pH of the produced water had been adjusted to 5.7 during field tests to protect the CTA FO membrane; FO draw solution and RO permeate samples had a similar pH due to the rapid diffusion of hydronium ions across each membrane.[17] Typical DOC concentration of the FO draw solution ranged from below 5 mg L^{-1} at system startup to 250 mg L^{-1} by the end of the week due to the closed loop operation. The DOC concentration in the RO permeate was consistently below 35 mg L^{-1}, regardless of increasing draw solution DOC concentration. Because the FO and RO membranes are tight and semipermeable, there is no TSS present in the draw solution or permeate. Salinity in the produced water feed, the FO draw solution, and the RO permeate was in the range of 18 g L^{-1}, 50 g L^{-1}, and 0.32 g L^{-1}, respectively.

The GC-MS TIC of three representative samples are shown in Fig. 2I–III. It should be noted that the TIC of draw solution and RO permeate are 400-times magnified compared to the produced water TIC. Therefore compound peaks are visible in the draw solution and RO permeate TIC that were hidden in the background or overlaid by more prominent peaks (*i.e.*, *n*-alkanes) in the produced water TIC. Individual *n*-alkanes are indicated in the produced water TIC (I) in Fig. 2. Results were not corrected in terms of compound specific recoveries during SPE.

3.2.1. Linear aliphatic hydrocarbons. For the purpose of this study, the concentrations of individual *n*-alkanes were summarized and are reported as the sum of *n*-C_{10} to *n*-C_{32}. *n*-Alkanes concentrations (sum of *n*-C_{10} to *n*-C_{32}) in the produced water feed of the FO–RO hybrid system were in the range of 2.3 to 28.8 mg L^{-1} as illustrated in Fig. 3. *n*-Alkanes concentrations measured in the draw solution and RO permeate after treatment were three orders of magnitude lower and ranged between 9.8 and 47.7 μg L^{-1} and 5.6 and 36.3 μg L^{-1}, respectively (Fig. 3). As the produced water was kept in large vented storage tanks until it was batch-fed to the FO–RO system, the slight decrease in *n*-alkanes in the produced water feed over time results most likely from biodegradation as well as volatilization of low molecular weight hydrocarbons. A multitude of microbes have been reported for the degradation of aliphatic hydrocarbons under aerobic and anaerobic conditions, using them as a source of carbon and energy. However, hydrocarbons differ in their susceptibility to microbial attack. Linear *n*-alkanes are more susceptible to microbial degradation than branched *n*-alkanes and small aromatic hydrocarbons. Some compounds (*e.g.*, high molecular weight PAH), may not be biodegraded at all.[18]

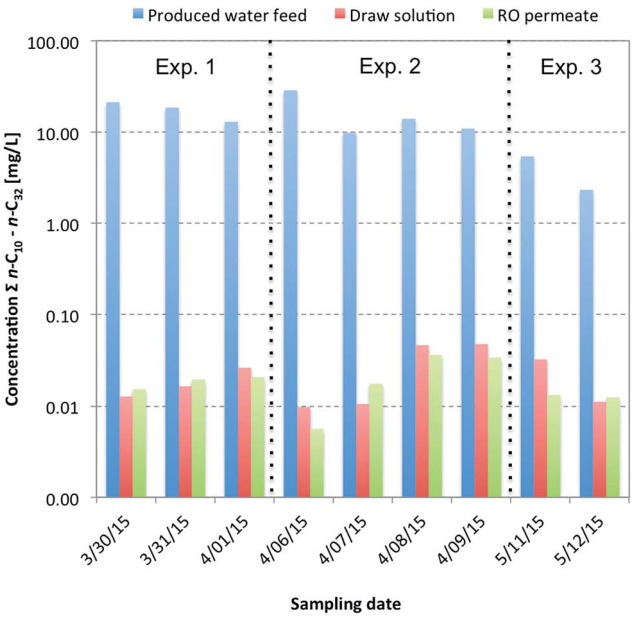

Fig. 3 Concentration of *n*-alkanes (sum of *n*-C_{10} to *n*-C_{32}) in the produced water feed, draw solution, and RO permeate of the pilot-scale hybrid treatment system during batch experiments 1, 2, and 3. Note logarithmic scale on the *y*-axis.

Treatment performance slightly decreased over the runtime of each experiment. This was likely due to increasing contaminant concentrations in the draw solution (closed loop), which result from the second tight membrane barrier of the RO system. Higher contaminant concentration in the RO feed (draw solution) in the long-term increased the driving force for permeation across the RO membrane. Nevertheless, treatment performance was restored after each membrane cleaning (every 3–4 days). During all three experiments, the removal efficiency of the overall system (after RO treatment) for *n*-alkanes was constantly better than 99.4% as shown in Fig. 4. Furthermore,

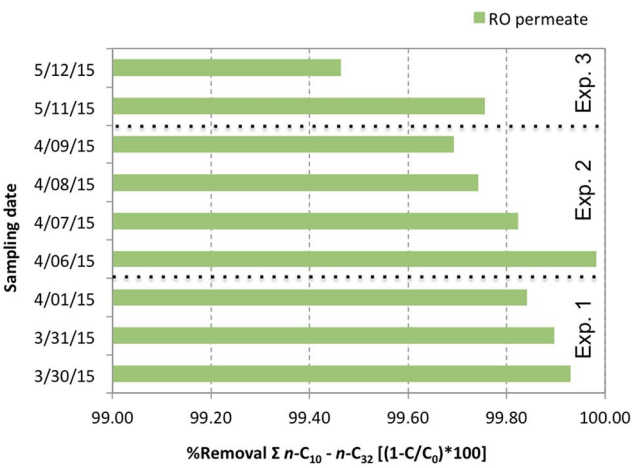

Fig. 4 Removal performance for *n*-alkanes (*n*-C_{10}–*n*-C_{32} range) during batch experiments 1, 2, and 3 by the pilot-scale FO–RO hybrid treatment system.

n-alkanes did not accumulate in the draw solution over the runtime of each experiment (Fig. 3), as the draw solution was not replaced in-between runs.

3.2.2. Polycyclic aromatic hydrocarbons. As described in Section 2.4, the 16 priority PAH were quantified in SIM mode. Non-detects of analyzed PAH in samples were set as half the MDL for statistical analysis and generating boxplots. Fig. 5 illustrates the eight PAH that were frequently detected above MDL in the produced water samples, namely naphthalene, fluorene, phenanthrene, fluoranthene, pyrene, benz(*a*)anthracene, chrysene, and benzo(*a*)pyrene. The black dashed line in Fig. 5 indicates their compound-specific MDL. The lower molecular weight PAH naphthalene, fluorene, and phenanthrene, which are relatively soluble in water compared to the high molecular weight PAH, were the most abundant PAH detected in the produced water feed, draw solution, and RO permeate – their concentrations in the produced water feed reached up to 359 μg L^{-1} (naphthalene), 40.7 μg L^{-1} (fluorene), and 68.3 μg L^{-1} (phenanthrene), respectively. Abundance and concentration of naphthalene, fluorene, and phenanthrene was significantly higher in FO draw solution compared to RO permeate (Fig. 5). As described in Section 2.5, CTA membranes were used for FO and TFC membranes for RO. While both membranes are semipermeable, the difference in their physiochemical characteristics can alter their rejection for the same compound.[19,20] High-pressure compaction of the RO membranes might also have led to higher rejection of PAH during RO treatment. Another aspect is that PAH potentially accumulate in the FO draw solution over the runtime of an experiment because draw solution is not exchanged until the membranes are due for maintenance cleaning. The brine can be disposed of in the same way as produced water, which is currently done through deep well injection. However, the brine volume is far less than the full volume of produced water that would have been disposed of.

Both acenaphthylene (2.1 μg L^{-1}) and anthracene (1.7 μg L^{-1}) were only detected in one out of nine produced water samples. Furthermore, they were not detected in the draw solution or RO permeate. Acenaphthene was not detected in any of the analyzed samples. Enrichment of 1 mL sample volume might not have been sufficient enough for detection of the high molecular weight PAH benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, indeno(1,2,3-*c*,*d*)pyrene, dibenz(*a*,*h*)anthracene, and benzo(ghi)perylene above detection limit in the produced water feed. Trace levels of these compounds were detected in the range of 0.4 to 0.8 μg L^{-1} in two samples of which 10 mL were enriched during SPE. However, none of them were detected in RO permeate samples of which 400 mL were enriched during SPE.

Individual PAH limits in drinking water have been established only for a few of them by the US EPA, European Union, and World Health Organization.[3] Naphthalene was the only analyzed PAH in RO permeate that exceeded the US EPA maximum contaminant level (MCL) of 0.2 μg L^{-1} for PAH in

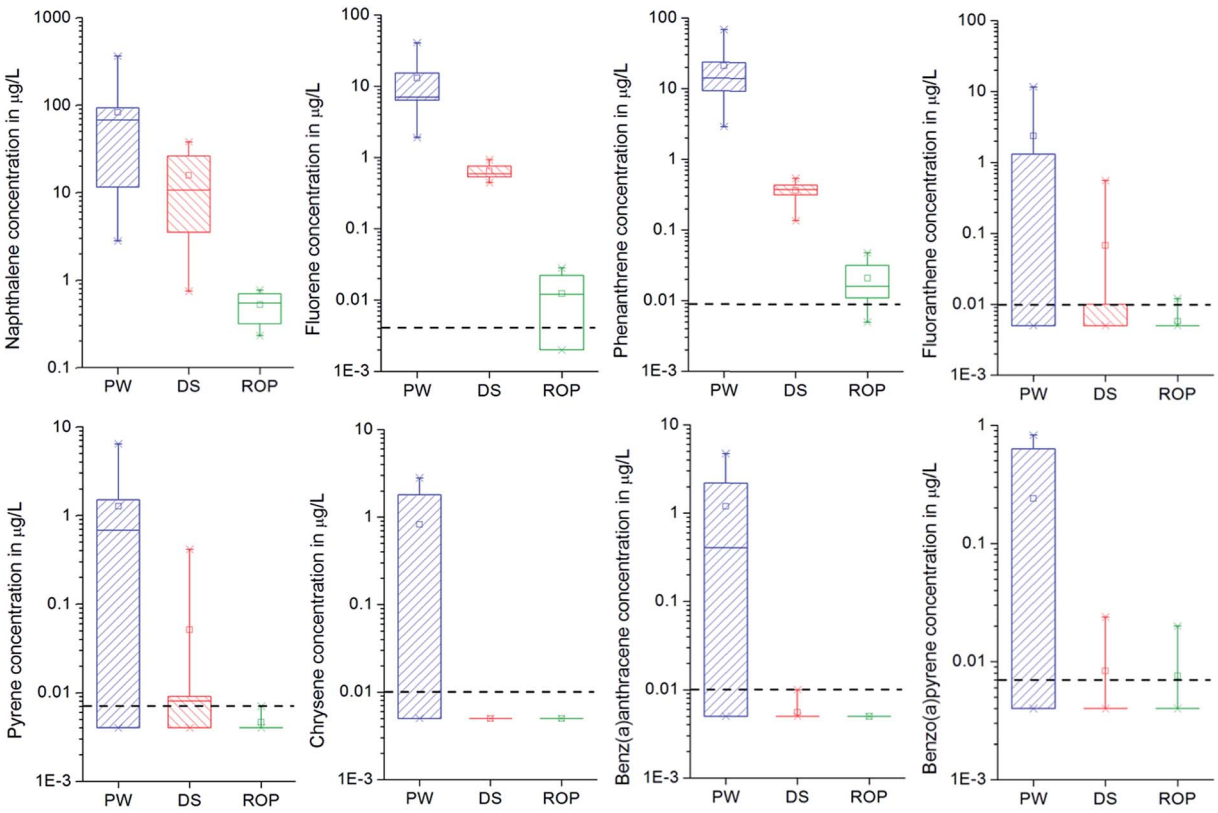

Fig. 5 Occurrence of eight selected PAH in the produced water feed (blue, $n = 9$), draw solution (red, $n = 9$), and RO permeate (green, $n = 9$) of the pilot-scale hybrid treatment system. Note logarithmic scale on the *y*-axis. Black dashed line indicates method detection limit.

drinking water. Naphthalene was present in RO permeate in the range of 0.2 to 0.8 μg L^{-1}, while concentrations of fluorene and phenanthrene were well below 0.05 μg L^{-1} in the RO permeate. Recently, risk limits for individual PAH in the aquatic environment were proposed by the Dutch National Institute for Health and Environment (RIMV).[21] Concentrations of naphthalene, fluorene, and phenanthrene in the RO permeate did not exceed RIMV's proposed maximum permissible concentration for aquatic ecosystems of 2.0, 1.5, and 1.1 μg L^{-1}, respectively. This implies several reuse options for the produced RO permeate if all inorganic and organic constituents are below established MCL: (1) the RO permeate, after pH adjustment and the addition of calcium and alkalinity, could be released into the environment as a valuable freshwater source under a valid discharge permit, (2) the RO permeate could be treated further by granular activated carbon filtration, chlorination, and post-treatment stabilization for non-potable or potable reuse, or (3) the RO permeate could be used as an industrial reuse stream by O&G companies (on-site reuse). Currently, the most viable option is industrial reuse due to the remote location of many O&G basins; however, increasing regulatory requirements will likely open new water reuse opportunities in industries beyond O&G exploration.

It is to be assumed that the higher molecular weight PAH were not truly dissolved in the produced water samples, which leads to an inhomogeneous distribution of these compounds in organic-rich and turbid samples (*e.g.*, thin film of non-aqueous phase liquid on top of produced water sample, settled out particles on the bottom of sample bottles) and possible losses during sample preparation if only small volumes of sample are enriched on the SPE cartridge. Samples were stored without headspace and subsamples of produced water feed were withdrawn from the same location in each sample – approximately 3 cm below the sample surface. The lower recovery rates of dibenz(*a*,*h*)anthracene and benzo(ghi)perylene during SPE compared to lower molecular weight PAH should be taken into account as well, although the high ionic strength of the samples substantially enhanced extraction efficiency.

4. Conclusion

SPE on disposable C_{18} cartridges followed by GC-MS was demonstrated to be a suitable procedure for the quantitative analysis of semi-volatile linear aliphatic hydrocarbons in the *n*-C_{10} to *n*-C_{32} range as well as 16 PAH in hydraulic fracturing wastewaters. The method can be applied for a broad range of water types. However, more research is necessary to develop strategies for a more standardized sampling and sample preparation procedure to allow the comparison of results among laboratories.

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