



Removal of organic compounds from shale gas flowback water

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ABSTRACT

Ozonation, sorption to granular activated carbon and aerobic degradation were compared as potential treatment methods for removal of dissolved organic carbon (DOC) fractions and selected organic compounds from shale gas flowback water after pre-treatment in dissolved air flotation unit. Flowback water was characterised by high chemical oxygen demand and DOC. Low molecular weight (LMW) acids and neutral compounds were the most abundant organic fractions, corresponding to 47% and 35% of DOC respectively. Ozonation did not change distribution of organic carbon fractions and concentrations of detected individual organic compounds significantly. Sorption to activated carbon targeted removal of individual organic compounds with molecular weight >115 Da, whereas LMW compounds remained largely unaffected. Aerobic degradation was responsible for removal of LMW compounds and partial ammonium removal, whereas formation of intermediates with molecular weight of 200–350 Da was observed. Combination of aerobic degradation for LMW organics removal with adsorption to activated carbon for removal of non-biodegradable organics is proposed to be implemented between pre-treatment (dissolved air floatation) and desalination (thermal or membrane desalination) steps.

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1. Introduction

The negative impact on the quality of surface and ground water is one of the major environmental consequences of shale gas production (Brantley et al., 2014; Ferrar et al., 2013; Jackson et al., 2013; Osborn et al., 2011; Vidic et al., 2013). Shale gas producers use a combination of horizontal drilling and hydraulic fracturing to recover gas from formations. Hydraulic fracturing implies high pressure well injection of large volumes of water mixed with inert solid material (proppant) and chemical additives. This mixture, called fracturing fluid, creates fissures in the shale increasing its permeability and gas recovery. The mixture of the injected fracturing fluid together with the connate water of the formation, which returns to the surface within few weeks after pressure being released, is called flowback water (Olmstead et al., 2013). The connate water of the formation, which continues flowing upwards for years after fracturing has been completed, is called produced

water (Vidic et al., 2013).

Both flowback and produced waters (FPW) are contaminated with high concentrations of total dissolved solids (TDS), oil and grease, natural radioactive materials (NORM), and dissolved organic matter (DOM) (Gregory et al., 2011). Injection into disposal wells was the most widely used shale gas wastewater management strategy until 2010 (EPA, 2016; Rahm et al., 2013). However, the limited availability of disposal wells, increased uncertainties about risks related to deep well injection, and legislative constraints make the industry turn towards reuse and discharge of FPW (Gregory et al., 2011; Mauter et al., 2014; Rahm et al., 2013; Silva et al., 2017). Removal of contaminants is required before FPW can be discharged. FPW reuse also requires removal of certain compounds, e.g. potential scalants and foulants. Treatment technologies typically include separation for removal of total suspended solids (TSS), oil and grease, adsorption for removal of organics, NORM and heavy metals, membrane or thermal desalination for TDS removal (Drioli et al., 2015; Igunnu and Chen, 2014; Jiménez et al., 2018; Saba, 2014). Desalination is a crucial step in the FPW treatment, because of the high TDS concentrations that often equal or exceed sea water salinity (Shaffer et al., 2013). Membrane and thermal

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desalination technologies for oil and gas produced water are well established and can remove TDS and majority of contaminants mentioned above (Abousnina et al., 2015; Fakhru'l-Razi et al., 2009). However, concentrations of organic carbon in shale gas FPW often exceed 1000 mg/L, causing fouling on the membranes and distillation equipment (Alzahrani and Mohammad, 2014; Chen et al., 2015; Thiel and Lienhard, 2014). In addition, desalination technologies are effective towards high molecular weight polar compounds, such as polycyclic aromatic hydrocarbons (PAHs), but poorly remove low molecular weight non-polar organics, that may also pose threats to the environment and human health (Annevelink et al., 2016; Butkovskiy et al., 2017; Ferrar et al., 2013; Shaffer et al., 2013). Despite that only few studies attempt to characterize the nature of organic compounds in FPW and evaluate potential treatment strategies for their removal (Butkovskiy et al., 2017; Camarillo et al., 2016).

Components of the fracturing fluid, including heterocyclic biocides, cocamidopropyl surfactants, ethylene glycol and derivatives, as well as natural constituents of shale, including aliphatic and aromatic hydrocarbons, alkanes, resins, asphaltenes, heterocyclic and halogenated organics were detected in FPW from U.S. shale basins using gas and liquid chromatography coupled to mass spectrometry (GC-MS and LC-MS) (Annevelink et al., 2016; Butkovskiy et al., 2017; Ferrar et al., 2013; Hayes, 2009; Lester et al., 2015; Maguire-Boyle and Barron, 2014; Orem et al., 2014). Lester et al. (2015) reported low removal of DOM from shale gas flowback water by advanced oxidation, whereas aerobic treatment removed >50% of DOM at flowback water TDS of 22.5 g/L. Other authors demonstrated that microbial mats are capable to decrease COD at TDS as high as 100 g/L (Akyon et al., 2015). Neither the fate of different DOM fractions nor the removal of individual organic compounds were studied in these works, moreover, Akyon et al. (2015) did their experiments with synthetic flowback water. Several authors reported high biodegradability of fracturing fluid components, including poly(ethylene glycol) surfactants and biocide glutaraldehyde (Kekacs et al., 2015; McLaughlin et al., 2016; Mouser et al., 2016). However, the degradation of compounds was studied in fracturing fluids, which composition is very different from FPW. High potential of granular activated carbon (GAC) for adsorption of fracturing fluid chemicals furfural and 2-butoxyethanol and powdered activated carbon (PAC) for adsorption of polyethylene glycols was also shown (Manz et al., 2016; Rosenblum et al., 2016). So far these are the only two studies focused on application of activated carbon for removal of organic chemicals from flowback water.

This paper aims to assess the removal of different fractions of dissolved organic carbon and individual organic compounds present in flowback water using typical primary treatment process (dissolved air flotation) followed by one of the common processes for organics removal (ozonation, adsorption to activated carbon or aerobic degradation). Flowback water is studied because, in comparison to produced water, this stream has typically high concentrations of organic carbon and contains potentially harmful components of fracturing fluids. The most promising treatment strategy for organic compounds removal is proposed and its integration with existing treatment processes is discussed.

2. Materials and methods

The shale gas flowback water was obtained from a Baltic shale gas basin (Poland) under non-disclosure agreement regarding location, storage conditions and composition of the fracturing fluid used at the production site. The water was sampled within two months after commencement of the first fracturing operation. It was transported in 20 L plastic containers and stored at 4 °C until

the experiments. The flowback water was pre-treated in a dissolved air flotation (DAF) unit assisted by coagulation in order to remove TSS, oil and grease. DAF-treated flowback water was used for ozonation, adsorption to GAC and aerobic degradation experiments.

2.1. Experimental set-up

2.1.1. Dissolved air flotation/coagulation

Flowback water ($V = 80$ L) was treated by FeCl_3 -assisted DAF in a stainless steel tank ($V = 200$ L). FeCl_3 (100 mg Fe/L) was added as a coagulant and pH was adjusted to 8.0 by addition of NaOH (0.5 g/L) (Megid et al., 2014). Flocculation was observed within 40 min and 3 L of water saturated with air was released to the stainless steel vessel from the adjacent pressurized tank ($p = 5$ bar). Flotation contact time was 10 min. DAF-treated flowback water ($V \approx 63$ L) was collected excluding precipitate and scum ($V \approx 20$ L) and stored at 4 °C until ozonation, GAC sorption and aerobic degradation tests were performed.

2.1.2. Ozonation

Ozonation was performed in batch mode in a glass vessel ($V_{\text{liquid}} = 2$ L) with ozone supplied through a bubble diffuser during 60 min. Ozone was produced from pure oxygen using a Fischer 503 ozone generator. The gas flow was maintained at 0.1 m³/h, and the ozone concentration in the reactor inlet at 6.3 g/m³. Ozone concentrations in the gas phase of the reactor inlet and outlet were measured by BMT ozone analyser 961TC and 961, respectively.

An ozone dosage of 0.3 g/L was applied to DAF-treated flowback water. Additionally, control tests with air supplied instead of ozone at the same flow rate were run to correct for volatilization. To correct for ozone losses in the system, a blank test with milliQ was run until stabilization of ozone concentrations in the reactor inlet (≈ 6.0 g/m³) and outlet (≈ 5.5 g/m³) has been reached. The ozone losses were taken into account when calculating ozone consumption of the flowback water. Liquid samples were filtrated through 0.45 μm pore size filters directly after the test and stored at -20 °C until the analyses.

2.1.3. Sorption to GAC

Sorption tests were performed with DAF-treated flowback water and three different types of GAC. Granular types of activated carbon were chosen because they are preferred to powdered by oil and gas industry due to lower carbon usage rates and operational costs (Arthur et al., 2005; Hackney and Wiesner, 1996). The tests were performed in stirred glass vessels ($V_{\text{liquid}} = 1$ L) using three different fresh GAC types typically used in municipal and industrial wastewater treatment, Chemviron F400, Norit GAC 830W and Norit C GRAN (Table S1) and dosage of 2000 mg/L. The adsorption tests were run for 6 weeks at 20 °C to reach the equilibrium state. Liquid samples were filtrated through 0.45 μm pore size filters directly after the test and stored at -20 °C until the analyses.

2.1.4. Aerobic degradation

Batch aerobic degradation test was adapted from OECD method 301A (OECD, 1992). The test was performed in triplicate in 250 mL glass bottles holding a liquid volume of 120 mL and headspace volume of 130 mL. Activated sludge adapted to high salinities was obtained from a wastewater treatment plant (WWTP) at Delfzijl (the Netherlands) which treats industrial wastewater with high Cl^- concentrations (2–20 g Cl^- /L) (van der Marel and de Boks, 2014). The sludge (volatile suspended solids (VSS) = 3.5 g/L) was collected from the aerobic nitrification basin and stored at 4 °C until the experiment. Sludge liquor had low COD (170 mg/L), no ammonium nitrogen and comparatively high chloride concentrations

(Cl⁻ = 22 g/L).

DAF-treated flowback water was mixed with sludge from Delfzijl WWTP (volumetric ratio of 0.29:0.71) to obtain the sludge loading of 0.1 g COD/g VSS*d. Diluted batch samples prepared for aerobic degradation experiments contained significantly lower COD (610 mg/L) and DOC (192 mg/L) when compared to the DAF-treated flowback water. Disodium phosphate was added as external phosphorous source to reach substrate N:P ratio of 5:1. The rest of the nutrients required according to OECD method 301A were present in the tested flowback water in excess. The glass bottles were closed with butyl rubber septa and incubated horizontally at constant temperature (20 °C) for 48 h on a linear shaker at 160 rpm for maximum oxygen up-take. The headspace composition was refreshed as soon as the oxygen volume fraction dropped to 10%.

To adapt the sludge to changes in salinity and substrate composition, batch incubations were repeated six times with the substrate refreshment between incubations. To refresh the substrate, the batches were centrifuged at 1500 rpm and the sludge pellet was mixed with a new portion of DAF-treated flowback water and sludge liquor. Full sampling campaign and analytical measurements were performed during the last incubation. The liquid samples and the headspace gas samples were taken at $t = 0.5, 1, 2, 3, 5, 7, 10, 24$ and 48 h. Headspace gas composition was analysed immediately after sampling. All liquid samples ($V = 1.5$ mL) were centrifuged at 10,000 rpm and the supernatant was stored at -20 °C until the analyses.

An abiotic control experiment was performed using DAF-treated flowback water and sodium azide (6.4 mg/L). Control batches were incubated and sampled similarly to the test batches.

2.2. Analytical measurements

Chemical oxygen demand (COD) and ammonium nitrogen (NH₄-N) were analysed with Hach test kits LCK-1414 and LCK-304 respectively. The pH was measured with Hach HQ 440d multimeter. VSS of sludge in aerobic degradation experiments were measured according to the Standard method 2540 D (APHA, 1998). Anions were analysed by ion chromatography with conductivity detector (IC-CD; Dionex ICS 2100). Cations were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent Vista-MFX) after acidification with 1% nitric acid. Volatile fatty acids (VFA) and alcohols were analysed by gas chromatography with flame ionization detector (GC-FID; Agilent 7890B) after sample acidification with formic acid. All samples were diluted with milliQ if the concentrations of analytes were above the calibration limits or salt concentration interfered with analytical procedures. The quantification limits for IC-CD, ICP-OES and GC-FID are presented in Tables S2 and S3.

Headspace gas composition in batch tests was analysed by gas chromatography with micro-thermal conductivity detector (GC- μ TCD; Shimadzu GC-2010). The concentration of oxygen in the headspace during biological batch tests was quantified according to ideal gas law with pressure inside the bottle measured by pressure meter (Greisinger GMH 3151). Specific oxygen uptake rate (SOUR) was calculated as a ratio of the measured oxygen consumption rate at the defined time period and sludge VSS.

The fractions of organic carbon were separated using size-exclusion chromatography (SEC) followed by multidetection of organic carbon (OCD), UV-absorbing aromatic and unsaturated structures at 254 nm (UVD) and organic bound nitrogen (OND; LC-OCD analysis at the DOC-Labor Dr. Huber laboratory). The detailed description of the analytical equipment and modified procedure for liquids with high TDS are found in the literature (Huber et al., 2011; Salinas Rodriguez, 2011). Calibration of molecular masses and detector sensitivities was performed with a NaCl-solutions of humic

and fulvic acids and potassium hydrogen phthalate. Chromatograms were processed on the basis of area integration using the program ChromCALC. The assignment of the DOC fractions detected in the flowback water is given in Supplementary material.

Organic compounds were analysed using Liquid Chromatography coupled to a Linear Ion Trap Orbitrap High Resolution Mass Spectrometer (LC-LTQ/HRMS) in positive and negative ionisation mode (see Supplementary material for additional methodological details) (Sjerps et al., 2016). Interpretation of detected peaks was performed using Sieve 2.2 (peak integration) in combination with Xcalibur software (molecular formula identification). The semi-quantitative concentrations of the attributed compounds were expressed as atrazine-d₅ equivalents (IS-eq) in positive ionization mode and as bentazone-d₆ equivalents in negative ionization mode with a detection limit of 0.05 μ g/L IS-eq. Confidence levels regarding the identification of compounds were reported according to (Schymanski et al., 2014). A level 5 confidence level suggests that an exact mass has been detected and an unequivocal molecular formula based on isotope and adduct information provides a level 4 identification. Level 3 suggests that a number of tentative structures are identified based on MS2 data. Levels 2 and 1 suggest that a probable structure or a confirmed structure has been assigned based on matches to library spectrums or reference standards. Total IS-eq concentrations of organic compounds were reported with a detection limit of 0.01 μ g/L. Carbon, hydrogen, oxygen, nitrogen and phosphorus were allowed for molecular formula determination and, if suggested by the spectrum, chlorine and/or sulphur were also considered. The direction (+ or -) of the internal standard mass error for a given spectrum in combination with isotope information (i.e. presence of sulphur, halogens, the number of carbons based on C¹³ information, etc.) was used to determine the most likely molecular formula. In addition, a suspect screening was also performed, using the Compound Discoverer 2.0 software (Thermo Scientific). The used suspect list includes chemicals that could potentially be present in shale-gas related waters and is described in detail in (Faber et al., 2017).

3. Results and discussion

3.1. Flowback water composition

The raw flowback water had a low pH (4.9) and high salinity (TDS = 103 g/L) with chloride being the dominating anion and sodium, calcium, magnesium and strontium – the dominating cations (Table S2). The relatively high concentrations of scale-forming cations (Ca, Mg, Sr and Ba) should be of concern when targeting flowback water reuse in hydraulic fracturing because of the high scaling potential (Thiel and Lienhard, 2014). Heavy metals were not detected in the flowback water, except for manganese, which concentrations were in the same order of magnitude as reported in the other studies (Hayes, 2009; Lester et al., 2015; Thacker et al., 2015; Ziemkiewicz and Thomas He, 2015).

The flowback water was also characterised by high COD (1800 mg/L), DOC (649 mg/L) and ammonium nitrogen (103.5 mg/L) concentrations. Fractionation of organic matter according to the size and hydrophobicity with subsequent detection of organic carbon, UV-absorbance at 254 nm and nitrogen showed that LMW acids and neutrals were two dominant organic fractions in the flowback water (Fig. 1; Table S4). Since UVD and OND detectors showed no response for elution of LMW neutrals, it was concluded that the fraction is represented by saturated hydrophilic compounds which do not contain nitrogen. GC-FID detection of VFA and alcohols has shown that LMW acid fraction was dominated by acetic acid (319 ± 19 mg/L, or 43%) and LMW neutral fraction – by ethanol (215 ± 17 mg/L, or 52%) (Fig. 1; Table S3). Other fatty acids

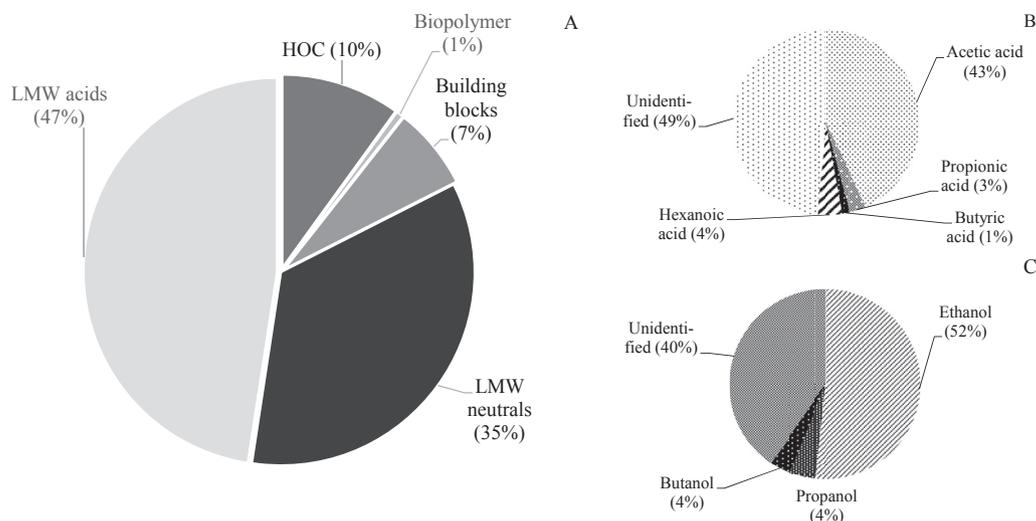


Fig. 1. Fractions of TOC (A) and molecular composition of LMW acid (B) and LMW neutral (C) fractions of the shale gas flowback water.

(propionic, butyric and hexanoic acid) and alcohols (propanol and butanol) were also detected, though in much lower concentrations (Table S3). Significant parts of LMW acids (48.6%) and LMW neutrals (40.5%) fractions were not classified further by GC-FID, suggesting the presence of a mixture of various LMW compounds apart from acetic acid and ethanol. Other DOC fractions included hydrophobic organic compounds (HOC), high molecular weight biopolymers ($M_w > 10000$ Da) and fraction of building blocks ($M_w = 300\text{--}500$ Da) (see Supplementary material for detailed description). These fractions presumably contain natural hydrocarbons of the formation and synthetic organic chemicals added to the fracturing fluid. However, the response of LC-OCD system to synthetic organic chemicals used in hydraulic fracturing was not tested since the composition of fracturing fluid used at the flowback water sampling site was not disclosed.

The concentration of acetic acid in this study (319 ± 19 mg/L) is in the range of the concentrations of acetate measured by Olsson et al. (2013) in flowback water from two hydraulically fractured wells in Germany (417 and 197 mg/L respectively). The same authors did not find acetate in a well which was not fractured, and concluded that acetate is a degradation product of polymers used in hydraulic fracturing fluids (Olsson et al., 2013). These results are also confirmed by other authors who observed release of organic acids from shale being in contact with fracturing fluid under high temperature and pressure conditions (Vieth-Hillebrand et al., 2017). Contrary, Orem et al. (2014) did not find significant concentrations of acetate in flowback water from hydraulically fractured wells in Marcellus and New Albany shales (USA). They suggest that acetate, even if formed downhole, will be immediately consumed by populations of methanogenic organisms in the well. According to these authors high concentrations of acetate in flowback water found at some fields can be explained by cracking of kerogens at temperatures exceeding 80°C , which also inhibits methanogens and thus the conversion of acetate to methane (Orem et al., 2014).

Presence of ethanol in shale gas flowback water was previously reported only in one study, where it was detected in one well out of nineteen and originated from fracturing fluid used at that location (Hayes, 2009). Ethanol may also be a degradation product of long-chain ethoxylated alcohols, which are frequently used in hydraulic fracturing operations.

Twenty-seven compounds with unique m/z ratios were detected in flowback water with LC-LTQ/HRMS at IS-equivalent

concentrations ≥ 0.05 $\mu\text{g/L}$ using Sieve 2.2 and Xcalibur software (confidence levels 2 to 5 according to Schymanski et al. (2014)) (Table S5). Molecular formulas were assigned to ten of these compounds allowing for a 5 ppm mass error. Several polyethylene glycol (PEG) oligomers (octaethylene glycol, decaethylene glycol, dodecaethylene glycol) and 1,6-dioxacyclododecane, 7,12-dione (cycloalkanedione) were semi-quantitatively detected in flowback water with confidence levels 2 to 4 (Table 1). PEG oligomers, which are common components of fracturing fluids, were previously detected in flowback and produced water from Denver-Julesburg Basin (USA) (Thurman et al., 2017). 1,6-dioxacyclododecane, 7,12-dione is detected in the fracturing fluid for the first time and most probably originates from alkanes naturally present in formation.

2-(2-butoxyethoxy)ethanol, possible transformation product of fracturing fluid additive 2-butoxyethanol, was the only compound identified by suspect screening at the concentration of 29.4 $\mu\text{g/L}$ IS-eq, being an evidence of downhole transformation of this frequently used and persistent fracturing chemical (Table 1).

High concentrations of easily degradable organic compounds, such as acetic acid and ethanol, indicate a potential for biological treatment. Moreover, combination of acetic acid as an energy-limited and ethanol as an energy-excess substrate should lead to higher bacterial growth rates and lower residual concentrations of organic matter (Babel, 2009).

3.2. DAF pre-treatment of flowback water

Pre-treatment of flowback water with DAF assisted by coagulation did not change COD and DOC significantly (4.2% and 0.4% removal respectively). However, removal of biopolymer fraction of DOC (74.1%) was observed, probably due to coagulation (Fig. 2). At the same time, increase of the HOC fraction was observed, probably because of the formation of metal-organic complexes which increase hydrophobicity of some organic compounds in flowback water. The pH increase from 4.9 to 8.0 caused by pH adjustment with NaOH required for coagulation has important implications for the following treatment steps. Neutral pH promotes biodegradation of organic matter compared to acidic pH of untreated flowback. The pH of the solution also governs the choice of activated carbon surface chemistry, since it may improve or impair removal of charged organic molecules (Al-Degs et al., 2008).

Table 1
Individual organic compounds detected in flowback water with the confidence levels 2 to 4 before and after treatment.

Identified name	CAS-nr.	Chemical formula	Level of confidence	m/z	Concentration in mg/L equivalent atrazin-d ₅				
					Flowback water	DAF effluent	Ozonation effluent	GAC effluent	Aerobic treatment, effluent
2-(2-Butoxyethoxy)ethanol possible	112-34-5	C ₈ H ₁₈ O ₃	2	162.1253	0.03	0.03	n.d.	n.d.	n.d.
	777-95-7	C ₁₀ H ₁₆ O ₄	4	201.1117	0.06	n.d.	n.d.	n.d.	n.d.
1,6-dioxacyclododecaan, 7,12-dione possible	2387-23-7	C ₁₀ H ₈ O ₃ S	4	207.0120	0.06	0.05	0.05	n.d.	n.d.
		C ₁₃ H ₂₄ ON ₂	4	225.1959	n.d.	n.d.	n.d.	n.d.	0.10
possible naphthalene sulfonate	1070663-76-1	C ₁₂ H ₂₆ O ₇	2	283.1744	n.d.	0.05	0.08	n.d.	n.d.
possible dicyclohexylureum	1985-57-5	C ₁₆ H ₃₄ O ₉	4	371.2267	0.05	0.06	0.13	n.d.	n.d.
possible hexaethyleneglycol	5579-66-8	C ₂₀ H ₄₂ O ₁₁	4	459.2792	0.07	0.09	0.24	n.d.	n.d.
possible octaethyleneglycol	162401-62-9	C ₂₄ H ₅₀ O ₁₃	2	547.3315	0.06	0.05	0.22	n.d.	n.d.
possible decaethyleneglycol									
possible dodecaethyleneglycol									

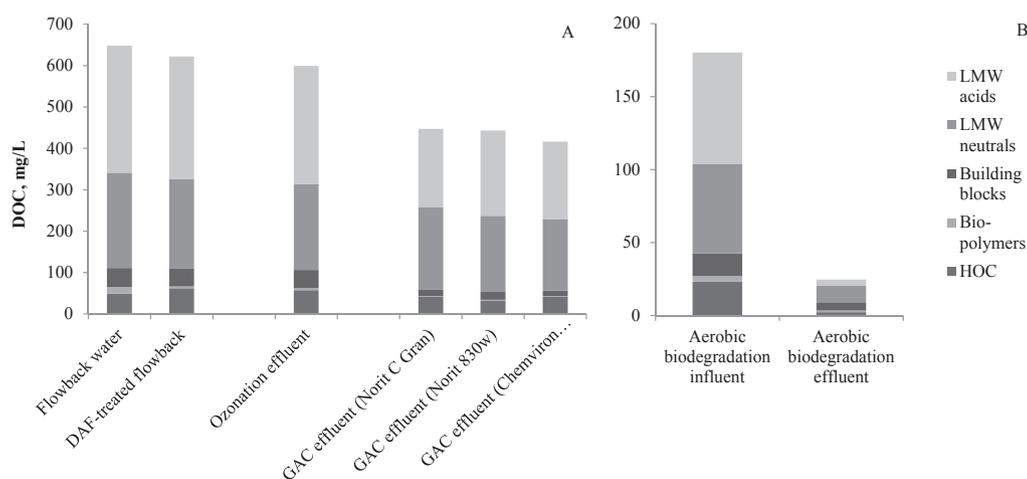


Fig. 2. Removal of different DOC fractions after DAF, ozonation, application of GAC (A) and aerobic biodegradation (B).

3.3. Application of ozone for flowback water treatment

The studied flowback water had low ozone demand with 44 mg O₃/L consumed during 60 min, whereas 300 mg O₃/L was applied. Foaming was observed at the beginning of the experiment, possibly caused by the presence of surfactants originated from fracturing fluid. COD and DOC removal was below 10%, as well as removal of different DOC fractions (Fig. 2; Table S4). Similar results were achieved by Lester et al. (2015) in the experiments with different advanced oxidation processes (UV/H₂O₂, O₂/H₂O₂, solar light/chlorine, photo-Fenton) treating shale gas flowback water. The authors have shown that OH radicals generated during ozonation were scavenged by bromide, present in the flowback water at high concentration. However, despite high bromide concentrations (570 mg/L) and pH neutralization during DAF pre-treatment, no changes in bromide concentrations were observed even at the highest ozone dosage applied in this study. Low efficiency of ozonation can be thus explained by saturated nature of organic compounds (von Gunten, 2003).

Indirect ammonium oxidation by the product of bromide ozonation, hypobromous acid (HOBr), is expected at Br⁻/N ratios above 0.4 (Eusebi and Battistoni, 2016; Tanaka and Matsumura, 2003). Thus, Eusebi & Battistoni (2016) removed >40 mg ammonium nitrogen applying ozone dosage similar to that applied in the present study (7.3 mg O₃/mg N) at high Cl⁻ (14 g/L) concentration and high COD (11 g/L). Despite the Br/NH₄-N ratio was equal to 4.4 in this study, no removal of NH₄-N was observed.

3.4. Application of GAC for flowback water treatment

COD and DOC removal with three studied GAC types did not exceed 25% (Fig. 2; Table S4). Biopolymers and building blocks were removed to the highest extent (67% and 58% respectively), whereas removal of LMW acids did not exceed 30% and removal of LMW neutrals was negative. A possible explanation is that most of the LMW organic compounds are weak adsorbates at near-neutral pH of DAF-treated flowback water, e.g. adsorption of acetate rapidly decreases at pH > 6.0 (Kipling, 1948). Moreover, displacement of LMW organic compounds with larger molecules might occur (Velten et al., 2011).

Chemviron F400 showed the best performance (23% COD removal and 20% DOC removal), followed by Norit C Gran and Norit 830w. Meanwhile, HOC removal was higher with Norit 830w (45% removal) than with two other carbon types (27% removal). This can be attributed to the differences in the carbon surface chemistry, hence Chemviron F400 and Norit C Gran have acidic surface whereas Norit 830w has alkaline surface (Table S1). Hydrophobic compounds with a negative charge would not be removed by GAC with acidic surface due to the repulsion forces observed at near-neutral pH of DAF-treated flowback water.

3.5. Application of aerobic degradation for flowback water treatment

The efficacies of the COD and DOC removal reached 73% and 83%

respectively after 48 h of incubation. (Fig. 2; Table S4). The COD was also measured in the liquid samples that were taken during incubation at 2, 5, 10 and 24 h showing that 71% removal was achieved already after 10 h of incubation. Further removal was not observed during next 38 h of incubation, indicating that $\approx 30\%$ of organic matter was non-biodegradable. Similar COD removal efficacies were observed by other researchers, who used activated sludge adapted to high chloride concentrations for flowback water treatment ($>50\%$ COD removal after 6 h of batch incubation) and conventional oil produced water treatment (81% COD removal after 21 h of aeration in SBR) (Lester et al., 2015; Pendashteh et al., 2010). SOUR during first hour of the incubation were between 25 and 40 mg/g VSS \cdot h (Fig. 3), indicating high biological activity of sludge (He et al., 2017). Further decrease of SOUR can be attributed rather to the substrate depletion in the batch experiment, than to the inhibition of bioactivity. Neither oxygen consumption nor COD removal were registered in the abiotic control batches (results not shown), indicating that observed removal is attributed solely to biodegradation.

Partial NH $_4$ -N removal (47%) was observed during first 10 h of incubation (Fig. 3). Theoretical amount of nitrogen, which could be assimilated in the batch experiment by biomass assuming 50% carbon assimilation and empirical bacterial composition CH $_{1.666}$ N $_{0.20}$ O $_{0.27}$ is equal to 18.1 mg/L. This value is close to the observed NH $_4$ -N removal of 17.6 mg/L after 10 h of incubation. Additionally, formation of NO $_2$, which is the main product of ammonium oxidation at high salinities, and NO $_3$ was not observed

(Cui et al., 2016; Vendramel et al., 2011). Therefore, nitrogen removal during aerobic treatment of flowback water occurs via assimilation by the biomass, and not via the nitrification.

Analysis of DOC in the flowback water and sludge liquor used for biodegradation experiments have shown that flowback water was the main source of organic carbon. Minimal possible removal of flowback water DOC fractions was calculated assuming that all DOC of sludge liquor is removed in biological experiments. The calculations showed high removal of DOC (79%) as well as its separate fractions (HOC, biopolymers, LMW neutrals and LMW acids) (Fig. 2; Table S4). GC-FID analysis of VFA and alcohols in the liquid samples taken during aerobic incubation showed complete removal of acetic acid within 1 h, whereas ethanol removal required 5 h of incubation. Catabolic free energy of ethanol oxidation ($-\Delta G^0 = 1325.5$ kJ/mol) is higher than that of acetate oxidation ($-\Delta G^0 = 893.7$ kJ/mol), which in turn leads to higher cell yields coupled to growth on ethanol and, in theory, preferable utilization of ethanol as a substrate (Rodén and Jin, 2011). However, first step of ethanol metabolism (oxidation to acetaldehyde) is endergonic, which limits bacterial catabolism of this substrate. Faster metabolism of acetic acid can be also explained by competitive inhibition of the ethanol catabolism by acetate.

3.6. Removal of individual organic compounds

Total IS-eq concentrations of the individual organic compounds detected in flowback water by LC-LTQ/HRMS in positive and negative ionization modes was 5.2 mg/L. Organic carbon makes up roughly 50% of the organic compounds, therefore, respective TOC is 2.6 mg/L (Mackinnon, 1981). This value is considerably lower than the organic carbon content of the building blocks fraction (46 mg/l) determined by LC-OCD analysis. Molecular weight of the compounds, which make up fraction of building blocks, is 300–500 Da, thus the fraction is completely covered by the LC-LTQ/HRMS molecular weight resolution of 115–1300 Da. Therefore, $<10\%$ of potentially present structures were identified by LC-LTQ/HRMS, either because of the analytical limitations of the chromatographic separation, or due to the high detection limits (0.05 μ g/L IS-eq).

DAF and ozonation did not improve removal of detected individual organic compounds, as shown by the IS-eq concentrations assigned to unique exact masses (Table S5) and total IS-eq concentrations (Fig. 4). 1,6-dioxacyclododecane, 7,12-dione was the only compound removed by DAF to <0.01 μ g/L IS-eq among 27 unique exact masses determined in flowback water (Table 1). Removal of this volatile cyclic polyester dimer was most probably achieved by stripping after pressurized air release. At the same time IS-eq concentrations of PEG oligomers in flowback water increased, possibly due to the breakdown of higher molecular weight PEG polymers (Table 1).

Application of GAC with acidic surface chemistry (Chemviron F400 and Norit C Gran) led to $>99\%$ removal of organic compounds (Fig. 4). Activated carbon with alkaline surface chemistry (Norit 830w) showed lower performance with 98% and 78% removal of organic compounds analysed in positive and negative mode respectively. These results are complementary to the observed removal of COD and DOC, which is higher for GAC with acidic surfaces (Fig. 2).

Removal of individual organic compounds detected in positive ionization mode did not change significantly in biodegradation experiments, whereas removal of the compounds measured in negative ionization mode decreased (Fig. 4). Organic compounds with higher molecular weight (Mw > 350 Da) were removed, whereas lower molecular weight compounds (Mw 200–350 Da) were formed after aerobic incubation (Table S5). These compounds

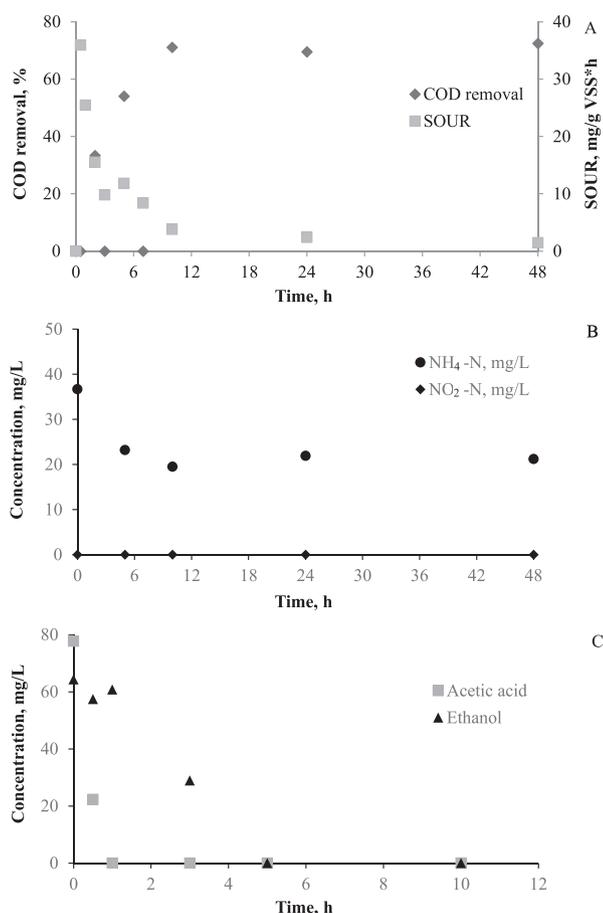


Fig. 3. COD removal and specific oxygen uptake rate (SOUR) (A), NH $_4$ -N and NO $_2$ -N removal (B), acetic acid and ethanol removal (C) during aerobic degradation experiments.

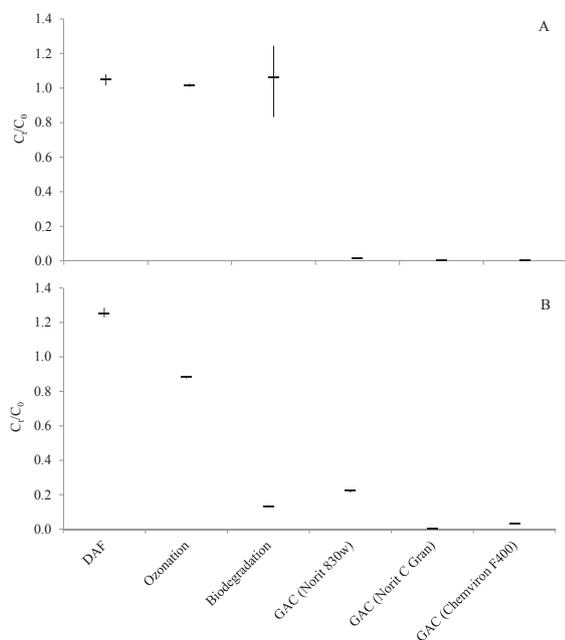


Fig. 4. The fraction of the organic compounds detected in positive (A) and negative (B) ionization mode (Ct/CO), which was left after DAF, ozonation, biodegradation and adsorption to GAC. The horizontal line represents the average total concentration ($n = 3$) and the vertical line - minimal and maximal concentrations.

can be identified as intermediates of aerobic degradation, because their presence was proved neither in the flowback water, nor in the sludge liquor. One of these intermediates was identified as 1,3-dicyclohexylurea. However it is unclear, whether the intermediates are resulting from biodegradation of compounds present in flowback water or sludge liquor.

The only compound, identified by the suspect screening, namely 2-(2-butoxyethoxy)ethanol, was not removed during DAF. The compound was removed by all subsequent treatments tested: ozonation, sorption to activated carbon and biodegradation. 2-(2-butoxyethoxy)ethanol is a transformation product of 2-butoxyethanol, which is frequently used in the fracturing fluids and is not rejected by membranes, therefore removal of this compound and its transformation products prior to membrane filtration is highly desired.

3.7. Implications for flowback water management

Aerobic biological treatment is inexpensive relatively to physicochemical processes for organic contaminants removal. However, it is rarely used for oil and gas produced water due to potential problems related to high salinity and presence of inhibitory compounds (Lefebvre and Moletta, 2006). Yet the present study together with the work of Lester et al. (2015) has shown that aerobic degradation targets easily degradable LMW organics that comprise the majority of organics in shale gas FPW. Yet, aerobic degradation at higher chloride concentrations than applied in this study (32 g/L) will be a challenging task (Akyon et al., 2015; Jiménez et al., 2018). Combination with other industrial wastewaters with lower salinities or adaptation of sludge to higher concentrations of Cl may be a solution for flowback waters with high salinities.

Whereas LMW organic acids and alcohols are removed by aerobic degradation, fractions with higher molecular weight are only partially removed, as shown by DOC fractionation and analysis of individual organic compounds. In contrast, activated carbon can

effectively remove compounds with Mw 115–1300 Da not affecting LMW organic acids and alcohols. Sorption to activated carbon is also efficient towards removal of other classes of organic pollutants, which commonly occur in shale gas FPW but were not detected in this study, namely PAHs, chlorinated organics and total petroleum hydrocarbons (Alzahrani and Mohammad, 2014; Pavoni et al., 2006; Rosenblum et al., 2016).

Hence combination of aerobic degradation with GAC filtration can target different fractions and classes of organic compounds. The processes can be applied as an intermediate treatment step between primary treatment and TDS removal in order to decrease membrane fouling, or prior to the direct flowback water reuse, if equipment fouling due to elevated concentrations of organic compounds is observed at the production sites (Alzahrani and Mohammad, 2014). Additional studies on the changes of flowback water toxicity during aerobic degradation and GAC filtration is needed, since only a small number of organic compounds can be identified using existing non-target screening methods.

Composition of shale gas flowback water differs significantly between production sites and even between wells within a single play (Shih et al., 2015). Hence, each full-scale application will require an individual approach, including characterization of flowback water and evaluation of its biological treatability. Flowback water may be combined with other types of industrial wastewater with lower salinity to offer optimal solutions for equalization of peaks in flow and composition, including salinity. Thus, environmentally safe discharge or re-use of such water streams may be facilitated, which is especially relevant for agricultural/industrial regions where water scarcity is paralleled by shale gas production.

4. Conclusions

The studied flowback water was characterised by the high concentrations of organic compounds, as indicated by COD (1800 mg/L) and DOC (649 mg/L) concentrations. Organic compounds in the studied flowback water were dominated by LMW acids and neutrals, with acetic acid and ethanol being the most abundant LMW compounds. Only a small number of individual organic compounds, including PEG-oligomers and presumable fracturing fluid additives 1,6-dioxacyclododecane, 7,12-dione and 2-(2-butoxyethoxy)ethanol were identified using non-target LC-LTQ/HRMS screening.

DAF applied for flowback water pre-treatment did not change COD and DOC, as well as concentrations of organic fractions and individual organic compounds significantly. This indicates necessity for specific organic removal, especially when the present organics cause fouling on the membranes frequently applied for TDS removal or on the drilling and fracturing equipment, when the water is going to be reused for the next fracturing operations without desalination step (Shaffer et al., 2013).

Ozonation was shown to be inefficient towards removal of organic compounds. Aerobic degradation removed >70% of DOC, mainly targeting LMW organics. In addition, GAC filtration removed fractions of DOC with higher molecular weight, including LC-LTQ/HRMS-detected individual organic compounds with molecular weight between 115 and 1300 Da. Combination of both technologies is proposed for efficient organic removal prior to desalination or flowback water reuse.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.03.041>.

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