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Establishing a link between composition and toxicity of offshore produced waters using comprehensive analysis techniques – A way forward for discharge monitoring?

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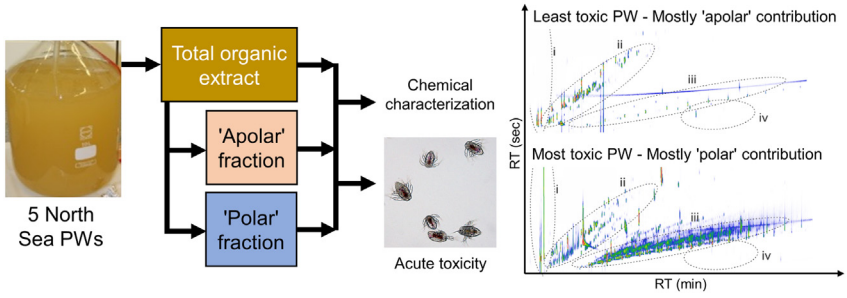
HIGHLIGHTS

- Produced water toxicity cannot be fully explained by standard analyte content.
- Both 'apolar' and 'polar' produced water compounds may contribute to toxicity.
- High-resolution mass spectrometry can help elucidate produced water composition.

GRAPHICAL ABSTRACT



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ABSTRACT

Extracts of produced waters from five mature Norwegian Sea oil fields were examined as total organic extracts (TOEs) and after fractionation into operationally-defined 'polar' and 'apolar' fractions. The TOEs and fractions were examined by gas chromatography (GC), GC-mass spectrometry (GC–MS), two dimensional GC–MS (GC × GC–MS) and liquid chromatography with high-resolution spectrometry (LC-HRMS) techniques.

Low molecular weight aromatics, phenols and other common petroleum-derived hydrocarbons were characterized and quantified in the TOEs and fractions. In addition, a range of more uncommon polar and apolar constituents, including those likely derived from production chemicals, such as trithiolane, imidazolines and quaternary amine compounds (so-called 'quats'), were tentatively identified, using GC × GC–MS and LC-HRMS.

The acute toxicity of the TOEs and subfractions was investigated using early life stages of the marine copepod *Acartia tonsa*. Toxicity varied significantly for different PW TOEs and subfractions. For some PWs, the toxicity was attributed mainly to the 'polar' components, while that of other PWs was associated mainly with the 'apolar' components. Importantly, the observed toxicity could not be explained by the presence of the commonly reported compounds only.

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Although, due to the vast chemical complexity even of the sub-fractions of the PW extracts, specific compounds driving the observed toxicity could be not be elucidated in this study, the proposed approach may suggest a way forward for future revisions of monitoring regimes for PW discharges.

1. Introduction

Produced water (PW) from the offshore oil and gas industry represents the largest volume waste stream into the marine environment worldwide (Lee and Neff, 2011). According to the Norwegian Environmental Agency (www.norskeutslipp.no), PW discharges on the Norwegian continental shelf have been between 150 and 190 million m^3 per year from 2008 onwards, representing on average ~1700 T of oil per year. This discharge is continuous, and volumes tend to increase as fields become more mature. The Norwegian oil and gas industry advocates ecological risk assessment as the basis for managing PW discharges to the North Sea (Lee and Neff, 2011), but currently only a small percentage of target compounds present in PW are included in these risk assessments.

PW quantities and composition varies greatly between wells, and are made up of a combination of the formation waters, dissolved or entrained oil and gas, and a wide variety of production chemicals (PCs). The latter are added to overcome operational problems, including corrosion, bacterial degradation, deposition in pipework, and emulsion formation (Kelland, 2009; Lee and Neff, 2011; McCormack et al., 2001).

Even after treatment to reduce the chemical and particulate load to meet regulatory requirements (typically monthly averages of 30–40 mg L^{-1} total oil and grease), the complexity of the remaining organic components in PWs represents a challenge in terms of identification and quantification. Such measurements are even more difficult following dilution of the PW in seawater: a dilution of 1:100 typically occurs within only a few tens of metres of the discharge pipes. Analysis of organic extracts directly from undiluted PW can help in identification and measurement of the PW chemicals before they spread in the environment.

Toxicity assessment studies with aquatic organisms, including fish, crustaceans, bivalves and bacteria has shown that PWs can elicit a range of acute and sublethal effects (Camus et al., 2015; Farmen et al., 2010; Hale et al., 2019; Henderson et al., 1999; Holth et al., 2008; Hylland et al., 2006; Neff et al., 2011; Sundt et al., 2009). While some studies, including those involving caged fish and bivalves, have shown that the acute effects of treated PW are substantially reduced when the discharge is diluted (Lee and Neff, 2011; Reed and Johnsen, 1996), others have shown that sublethal effects may still be a risk following PW dilution. For example, Meier et al. (2010) showed that PW exposure clearly had effects on the development of Atlantic cod (*Gadus morhua*) larvae, where exposure to 1% PW after hatching resulted in a failure to begin feeding and death by starvation. This inability to feed may be linked to the increased incidence of jaw deformities seen in these larvae. A recent study confirmed developmental and also found cardiotoxic effects of diluted PW to both Atlantic cod and haddock (*Melanogrammus aeglefinus*) embryos (Hansen et al., 2019). The causative agents in the most toxic PWs are still unknown (Karman and Reerink, 1998; Lee and Neff, 2011; Meier et al., 2010; Reed and Johnsen, 1996). A more comprehensive knowledge of PW composition is therefore required if the long-term ecological effects of PW discharges are to be better understood and regulated.

Common organic constituents of PWs (e.g. aromatic hydrocarbons, phenols, simple short chain acids) and some commonly used PCs, can be identified and are quantified routinely by gas chromatography coupled to mass spectrometry (GC–MS) and liquid chromatography coupled to MS (LC-MS) (Brown et al., 1992; Harman et al., 2011; Lee and Neff, 2011; Reed and Johnsen, 1996; Røe Utvik, 1999; Tibbetts et al., 1992). However, PWs also comprise large numbers of lesser known, or unknown, organic compounds. Furthermore, the operational challenges associated with maturing oil and gas fields often necessitate deployment of different and novel PCs to help maintain flow and productivity (Kelland, 2009; McCormack et al., 2001; NOROG, 2017). Identification and quantification of these, lesser known, compounds in PW is challenging and requires advanced methods of analysis. The application of multi-dimensional chromatography coupled to mass spectrometry (e.g. GC × GC–MS) and high-resolution MS (HRMS) have been proposed and demonstrated useful for elucidation of chemical composition of such complex mixtures as petroleum and PW (He et al., 2017; Melbye et al., 2009; Oetjen et al., 2017; Rowland et al., 2011; Thurman et al., 2017; Wang et al., 2013). Combining GC and LC based methods offer the opportunity to study a wider range of 'polar' and 'apolar' chemicals in PW, whether they originate from petroleum (Robson et al., 2017), or from PCs (McCormack et al., 2001). GC × GC–MS allows significantly higher chromatographic resolution and identification of complex mixtures amenable to GC, including even some 'polar' compounds if derivatisation is first employed (e.g. naphthenic acids (NA) (Wilde et al., 2015)), while LC-based methods are more applicable for non-derivatised 'polar' or non-GC-amenable contaminants. Monitoring of the compositions of PW from mature fields by such methods may be revealing and may help to guide future environmental monitoring protocols (Samanipour et al., 2018).

The aim of the current study was to develop tools to identify 'novel' compounds in PW that may contribute to PW toxicity and should thus be part of routine discharge monitoring programs. A novel approach aiming to identify compounds or compound groups with significant contribution towards PW toxicity is demonstrated. The total organic extracts (TOEs) and 'polar' and 'apolar' sub-fractions of a suite of PWs were used to investigate which chemical components might be contributing to at least some of the PW toxicity. PW samples were collected from five Norwegian North Sea oil platforms representing mature oilfields producing different oil types (namely asphaltenic, naphthenic and waxy oils). The PW TOEs were subjected to a detailed analytical chemical characterization using a combination of GC–MS, GC × GC–MS and LC-HRMS techniques. In addition, the acute toxicity of each TOE and the respective 'polar' and 'apolar' sub-fractions was determined using a simple modified ISO 14669 (LC_{50} 48 h) test on nauplii of the marine copepod *Acartia tonsa*. The aim is that the combined composition and toxicity evaluation protocol can help in identifying compound groups of concern that should be routinely monitored in PW effluents.

2. Materials and methods

2.1. Chemicals

Certified alkane, decalin, polycyclic aromatic hydrocarbon (PAH), alkylated PAH, phenol, alkylated phenol and deuterated phenol and PAH reference standards were purchased from Chiron AS (Trondheim, Norway). Calibration, surrogate and recovery standards were all prepared by dilution of compounds in dichloromethane. All solvents were of analytical grade (Sigma-Aldrich, VWR or Thermo Fisher Scientific).

2.2. PW sampling, extraction and fractionation

Samples of PW were supplied by oil production companies operating on the Norwegian shelf. PW was collected from platforms located on five mature Norwegian North Sea oil fields. These oil fields were

selected as they represent a range of different crude oil types, including asphaltenic, naphthenic and waxy crude oils. PW samples (7–28 L) (Table S1, Supporting information (SI)) were taken at offshore facilities during periods of normal operation. Samples were transferred to Teflon lined bags and shipped to the onshore laboratory for further processing (Fig. 1).

Upon arrival in the onshore laboratory, the samples were immediately acidified (HCl, pH <2) to prevent degradation and facilitate extraction of acidic compounds. For chemical characterization, a 0.5 L subsample of each PW was extracted using dichloromethane (DCM) *with* the addition of surrogate internal standards (naphthalene-*d*8, acenaphthene-d10, phenanthrene-*d*10, chrysene-*d*12, perylene-*d*12, phenol-*d*6, *p*-cresol-*d*8 and 4-*n*-propylphenol-*d*12) to account for target analyte losses during the extraction step. The extract was dried over anhydrous sodium sulphate and concentrated by gentle solvent evaporation. For use in toxicity studies, and for further fractionation, the remaining bulk PW samples were extracted *without* addition of internal standards to create a "PW total organic extract (TOE)" for use in advanced chemical characterization, fractionation and toxicity tests.

A sub-sample of each PW TOE was subject to fractionation into so-called 'polar' and 'apolar' fractions. Silica SPE columns (Agilent Bond Elut SI, 500 mg) were conditioned with *n*-hexane and the PW TOEs transferred to the column. The 'apolar' fraction was defined as that which eluted with one column volume of *n*-hexane, followed by one column volume of DCM. The 'polar' fraction was defined as that collected by gradient elution using increasing amounts of methanol (5–20%) in DCM. All TOEs and 'polar' and 'apolar' fractions were stored dark and frozen (−20 °C) prior to advanced chemical characterization and use in toxicity tests.

2.3. Acute toxicity testing

Toxicity exposure stock solutions were prepared by reconstituting the TOEs, 'polar' or 'apolar' fractions in seawater to a nominal concentration of 300 mg L^{-1}. The appropriate amount of TOE, 'polar' or 'apolar' fraction, dissolved in DCM, was added to a volumetric flask using a gas tight syringe. The DCM was then removed by evaporation to dryness at 35 °C under a very gentle flow of N_2 gas (10 min). Once dry, the flasks were filled with sterile-filtered (0.2 μm) seawater at room temperature, and re-dissolution of the dried extract was assisted by immersion in a sonication bath (3 × 5 min). Solvent controls with the corresponding volume of DCM were also prepared.

The acute toxicity of all TOEs and 'polar/apolar' subfractions was determined using a modified version of the standard ISO 14669 (LC_{50} 48 h) test which employed nauplii of the marine copepod *Acartia tonsa*. All assays were performed with the same number of vessels and a dilution series ranging from the undiluted reconstituted exposure stock solution (100%) to 4% in seawater with a spacing factor of 1.7 and four parallel vessels for each dilution. In addition, a negative control with clean seawater (8 vessels) and a positive control with 1.0 mg L^{-1} 3,5-dichlorophenol (4 vessels) were prepared. At the start of the exposure, nauplii from a 2–3 day post hatch culture were gently concentrated on a 40 μm sieve partially submerged in filtered sea-water before a subsample of nauplii was transferred to each exposure solution (30 mL) in a glass crystallization dish (diameter = 75 mm) in 125 μL of sea-water. This to avoid dilution of the exposure solution while still ensuring that nauplii were added in excess to populate the four replicate exposure vessels without further dilution of the solution. Batches of approximately 20 nauplii were collected from the dish by pipetting under a dissecting microscope, gently transferred to glass vials (5 mL), which were filled to the neck with exposure solution and capped. The vessels were left in a temperature-controlled room at nominal temperature of 20 ± 2 °C under a 16:8 (light:dark) light regime at an intensity comparable to the culturing conditions. Lethality after 48 h was recorded under a dissecting microscope and nauplii not responding to tactile stimuli by the tip of a pipette were scored as lethal immobilised.

2.4. Chemical characterization – target component analysis

The PW TOEs, 'polar' and 'apolar' fractions and reconstituted seawater solutions used for toxicity testing, were analysed for decalins, PAHs, alkylated PAHs and C_{0-9} phenols (the total analyte list is shown in Table S2, SI) using GC–MS, and for GC-amenable total extractable matter (TEM) using gas chromatography-flame ionisation detection (GC-FID). Surrogate and recovery (fluorene-*d*10) internal standards were added to the samples prior to analysis. GC-FID analysis was conducted with an Agilent 7890A GC fitted with an Agilent HP-5MS UI column (30 m × 0.25 mm × 0.25 μm) and the carrier gas was helium at a constant flow of 1.5 mL min^{-1}. Samples (1 μL) were injected at 330 °C by pulsed splitless injection. The oven programmed from 40 °C (1 min hold), then ramped to 315 °C at 6 °C min^{-1} (15 min hold). For GC–MS analysis, an Agilent 7890B GC coupled with an Agilent 5977A quadrupole MS was used. The GC-column was an Agilent HP-5MS UI (60 m × 0.25 mm × 0.25 μm) and the carrier gas was helium at a constant flow of 1 mL min^{-1}. Samples (1 μL) were injected at 325 °C by pulsed splitless injection. The oven was programmed from 40 °C (1 min hold), ramped to 220 °C at 6 °C min^{-1} and then ramped to 325 °C at 4 °C min^{-1} (15 min hold). The transfer line temperature was 300 °C, the ion source temperature was 300 °C and the quadrupole temperature was 165 °C. The electron ionisation (EI) source was operated at 70 eV. Analysis was performed in both full scan (50–500 *m*/*z*) and selected ion monitoring modes. Quantification of target compounds was performed using the average response factors (RF) of the parent PAH or phenol compounds.

2.5. Chemical characterization – non-target component analysis

Acidic compounds in the extracts and fractions were first derivatised with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSFTA). An excess of the silylating reagent was added to samples, which were then sealed and heated for ~1 h (70 °C). The excess BSTFA was then removed under N_2 (30 °C) and the derivatised samples reconstituted in an appropriate solvent and analysed immediately.

Derivatized acids analyses were conducted on an Agilent 7890A GC coupled with an Agilent 5975A MS. The GC-column was an Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm), and the carrier gas was helium at a constant flow of 1 mL min^{-1}. Samples (1 μL) were injected at 250 °C by splitless injection. The oven was programmed to 40 °C for 1 min (1 min hold) then ramped to 300 °C at 10 °C min^{-1} (10 min hold). The transfer line temperature was 300 °C. Individual compounds were identified by total ion current (TIC; *m*/*z* 50–500 mass range) with a constant ionisation potential (70 eV). System suitability was routinely checked using the internal calibration procedure and the perfluorotributylamine (PFTBA) calibration compound.

Comprehensive two-dimensional gas chromatography–mass spectrometry (GC × GC–MS) analyses were performed using a 7890A GC interfaced with a Zoex ZX2 GC × GC cryogenic modulator and a Markes/Almsco BenchTof dx™ time of flight mass spectrometer. The first-dimension column was a 100% dimethyl polysiloxane Rxi®-1 ms (60 m × 0.25 mm × 0.25 μm), followed by a 1.5 m × 0.25 mm deactivated fused silica modulation loop. The second-dimension column was a 50% phenyl polysilphenylene siloxane SGE BPX50 (2.5 m × 0.25 mm × 0.25 μm). The oven was programmed from 35 °C (1 min hold), ramped to 150 °C at 5 °C min^{-1}, then to 350 °C at 1.7 °C min^{-1} (10 min hold). The hot jet was programmed to a temperature of 115 °C (1 min hold), heated to 230 °C at 5 °C min^{-1}, then to 400 °C at 1.8 °C min^{-1}. The secondary oven was heated from 95 °C (1 min hold) to 210 °C at 5 °C min^{-1}, and finally to 350 °C at 1.6 °C min^{-1}. The modulation time was 4 s with a 180 ms pulse length. Helium carrier gas was used (constant flow; 1.0 mL min^{-1}) and samples (1 μL) were injected at 275 °C by splitless injection. The MS transfer line temperature was maintained at 330 °C. Mass spectrometric parameters were as follows: ionisation energy 70 eV, scan speed 50 Hz, recorded mass range

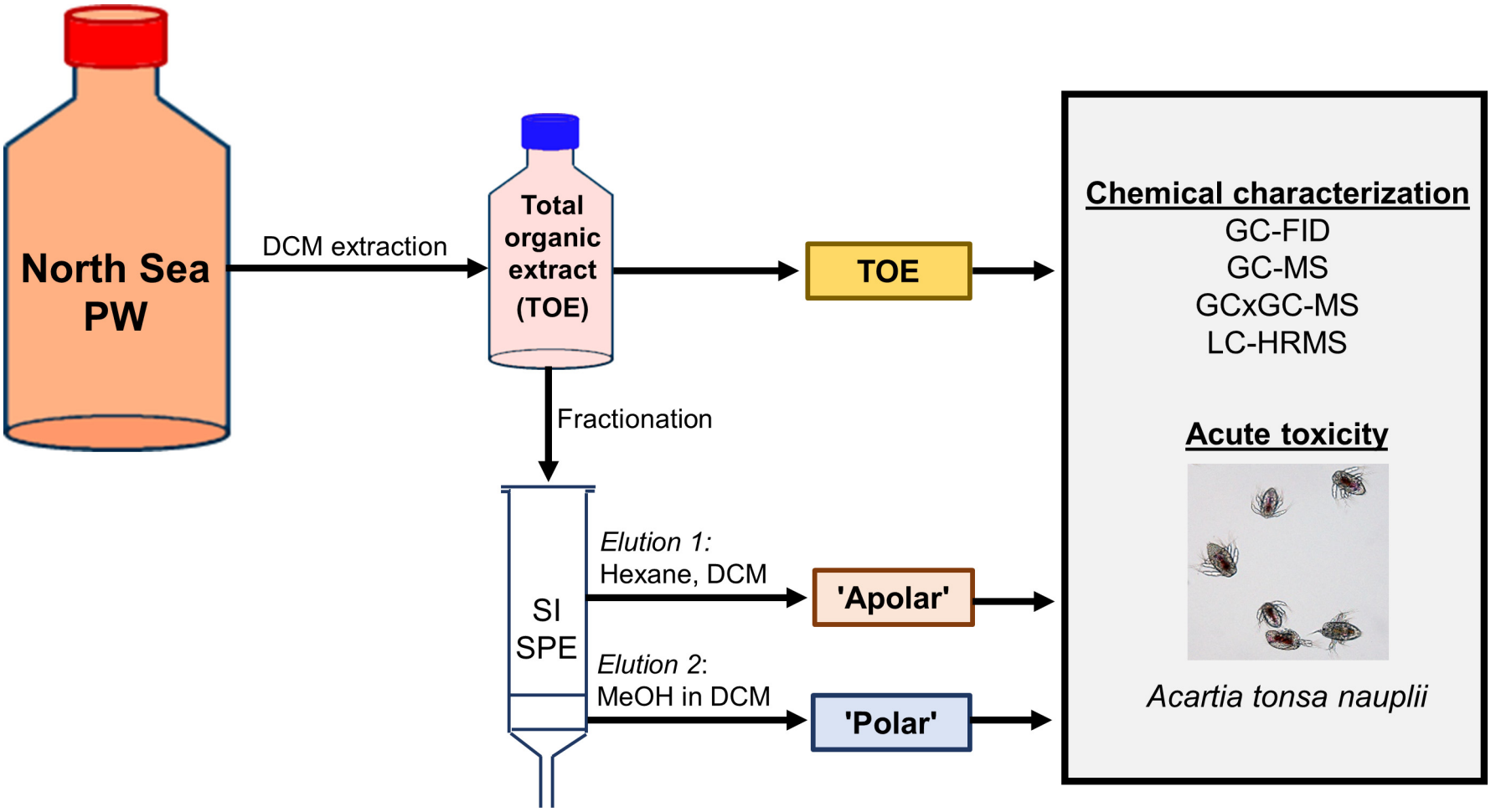

Fig. 1. Overview of sample processing from receipt of the produced water (PW), through extraction, fractionation, chemical characterization and toxicity testing.

50–550 *m/z*. Data were collected in ProtoTof (Markes International, Llantrisant, Wales, U.K.). System suitability was routinely checked using the internal calibration procedure and the PFTBA calibration compound.

GC Image v2.3 (Zoex, Houston, TX) and ChromSpace (Markes International Limited, Llantrisant, Wales, U.K.) were both employed in the processing and presentation of GC × GC–MS data. Both of these software packages provide largely the same functionality, presenting chromatograms as two-dimensional colour contour plots, with the ability to create personalised colour schemes, generate extracted ion current (EICs) chromatograms, to compare mass spectra to library spectra and to generate 3D images. EICs were created by applying additional constraints (such as retention time (RT) windows and relative or absolute abundance of specific ions within the chromatograms) using built-in software features ('CLIC expression' in GC Image, or 'Parametric filtering' in ChromSpace).

A liquid chromatography-mass spectrometry (LC-MS) investigation of the TOEs for non-target compounds was carried out using a high-resolution accurate-mass (HRAM) Orbitrap mass spectrometer. LC-MS was performed using a U3000 UHPLC liquid chromatography system coupled to a Q Exactive Focus mass spectrometer fitted with a heated electrospray ionisation source (HESI II). Data were acquired using Xcalibur 4.0.27.19 software (Thermo Scientific, Hemel Hempstead, UK). The LC column was an ACE 2.5 UltraCore 2.5, Super C18 (100 × 2.1 mm, 2.5 μm, Advanced Chromatography Technologies Ltd., UK). A three eluent gradient system was used as follows: Eluent A) 0.1% formic acid (FA) in water; B) 0.1% FA in acetonitrile and C) 0.1% FA in propan-2-ol, with a gradient elution profile [time (min)/ A:B:C (%)]: 0/90:10:0 → 17/15:85:0 → 20/5:75:20 → 24.5/0:10:90 → 27/0:10:90 → 27.1/90:10:0 → 30/90:10:0. Separations were carried out at 50 °C with an eluent flow rate of 500 μL min^{-1}. Injection volume was 10 μL with a needle wash of methanol. The mass spectrometer conditions were: nitrogen sheath and auxiliary gas (60 and 20 Arbitrary units, respectively), vaporiser temperature (425 °C), spray voltage (+3500 V), capillary temperature (325 °C) and S-lens RF level (50). Data were collected in the positive ion, full MS-all ion fragmentation mode (FS-AIF, MS and MS/MS data collected) for full scan mass range (*m/z* [100 −1000]) with a resolution at 70,000 at *m/z* 200, AGC target (1e6, automatic gain control), maximum ion time (auto) and micro scans (1). For the MS/MS (AIF) the mass range (*m/z* [100–1000]) and resolution at 70,000 (*m/z* 200), AGC target (3e6), maximum ion time (auto), micro scans (1) and a stepped collision energy (ce: 15, 30 and 45 eV) were used. External mass calibration (≤3 ppm) was used with autocalibration using Pierce LTQ Velos ESI positive ion calibration solution (n-butylamine, caffeine, MRFA, and Ultramark 1621 (Thermo Fisher Scientific, UK)). Data processing, including obtaining mass spectra, generating TIC chromatograms, EIC chromatograms, creating chromatographic figures and prediction of chemical formulae (max elements; ^{14}N (10), ^{16}O (15), ^{12}C (13), ^{1}H (60), ^{32}S (10), ^{35}Cl (4) and ^{31}P (10)) was manually conducted using FreeStyle 1.4 software (Thermo Fisher Scientific, UK) typically using default parameters.

2.6. Statistics

The lethal concentrations (LC_{10} and LC_{50}) were calculated by a non-linear Sigmoidal dose-response model with variable slope (four-parameter logistic equation) using GraphPad Prism version 5.0b for MacIntosh (GraphPad Software, San Diego California USA).

3. Results and discussion

Discharges to the sea (e.g. PW and PC) and emissions to air, from all oil fields on the Norwegian Continental Shelf are annually reported in detail by the operating companies to the Norwegian Environment Agency. These reports are available online (www.norskoljeoggass.no) and contain detailed data on the composition of PW. Here, we performed both standard and advanced chemical analyses, and toxicological assessments on extracts from five oil platforms. Rarely are such data reported since regulations normally require only chemical analysis of a set of standard compounds and groups. Given the amounts of PW discharged into the Norwegian Sea annually (150 to 190 million m^3; www.norskeutslipp.no), the samples of a few litres (7–28 L) used in the current study of course only provide (though rare), 'snapshots' of PW composition and any associated toxicity. In general, standard analysis of total hydrocarbons performed in the current study were in accordance with reported "oil-in-water" discharges from the platforms during the period of operation when samples were provided to SINTEF. Minor variations could be caused by several factors, such as temporary problems with the water treating systems, removal or replacement of PC, and new wells coming into production.

3.1. Produced water fractionation and acute toxicity

The methodology applied for extraction, fractionation and reconstitution of PW solutions for toxicity testing was designed to be efficient and reproducible. Extraction of acidified water samples by DCM is considered one of the more efficient sample preparation procedures with generally high recovery of a range of compound groups relevant to PW (Hughes et al., 2017; Samanipour et al., 2018).

The repeatability of the fractionation was 5% relative standard deviation (RSD) in total extracted GC-amenable organic matter (TEM) for the 'polar' fraction and 2% RSD for the 'apolar' fraction ($n = 5$). Between 75 and 85% of the total extracted GC-amenable TEM was recovered in the two fractions compared with simple extraction with DCM (Fig. 2).

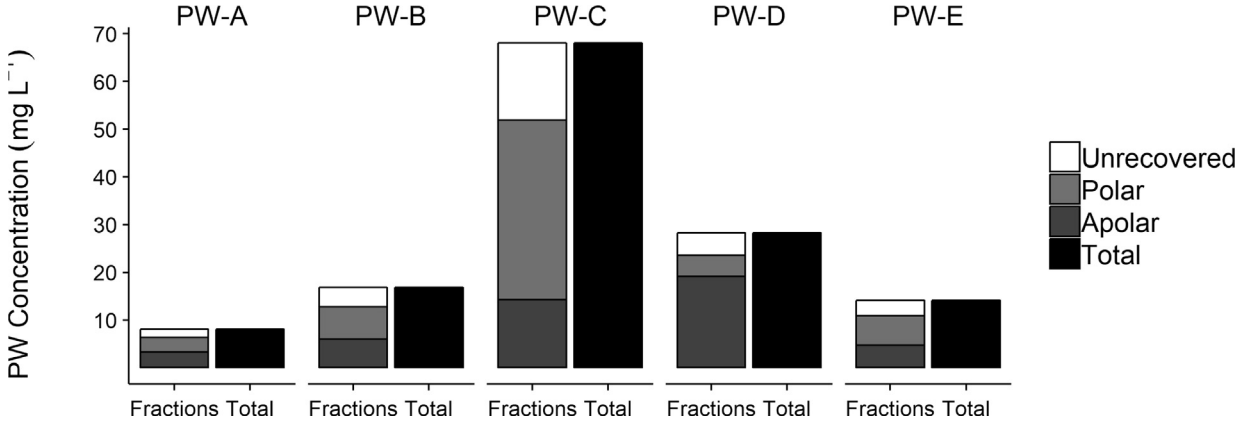

Fig. 2. Concentrations of the GC-amenable total extractable matter (TEM) compounds in PW total organic extracts (TOEs) and the 'apolar', 'polar' and unrecovered TOE fractions, compared to the TOEs obtained by simple extraction with dichloromethane.

Of the total GC-amenable compounds, PW-C produced an extract with the highest concentration (68 mg L^{-1}), followed in decreasing order by extracts of the PW-D (28 mg L^{-1}), PW-B (17 mg L^{-1}), PW-E (14 mg L^{-1}) and PW-A (8 mg L^{-1}) PWs (Fig. 2). Reflecting their known chemical properties, some PWs had higher proportions of compounds defined by normal phase silica fractionation as 'polar' (e.g. PW-C, 72%), while others had a higher content of 'apolar' compounds (e.g. PW-D, 81%) (Fig. 2). In PW-B, PW-E and PW-A extracts, the relative recovered contents of 'apolar' and 'polar' compounds were approximately equal (~45–55% of each fraction).

An inherent feature of the re-constitution protocol for production of the PW solutions used to measure acute toxicity, was the loss of volatile compounds, including naphthalenes, small monoaromatic compounds and some phenols, from the PW extract and fractions. The resulting solutions would therefore be somewhat depleted in the latter and enriched in semi- or non-volatile PW compounds, compared with the TOEs.

Of the five tested PWs in the current study, three different acute toxicity distribution patterns were observed (Table 1). For the PW-B and PW-E, the toxicity was mainly attributed to the 'apolar' fraction, while for PW-D and PW-C, the toxicity could be attributed mainly to the 'polar' fraction. PW-A produced a considerable contribution to toxicity from both fractions. In relative order the acute toxicities could be summarised as:

Total PW : PW−B>PW−C>PW−A>PW−D>PW−E

'Apolar' : PW−B>PW−A>PW−E>PW−C>PW−D

'Polar' : PW−B>PW−D>PW−A>PW−C>PW−E

3.2. Produced water chemical characterization

Fig. 3 shows the concentrations and profiles of routinely (GC–MS) monitored target compounds (Faksness et al., 2004; NOROG, 2012) in the five TOEs of the PWs and their 'polar' and 'apolar' fractions. The relative phenol contents of the PW-A, PW-E and PW-B were high compared to the PW-C and PW-D. The PW-C had a profile of decalin, naphthalene and 2–3 ring PAH hydrocarbons that were similar to many crude oils. In contrast, the PW-D extract was dominated by naphthalenes and lower molecular weight phenols. Such distributions of oil-derived components in PWs are well known (Faksness et al., 2004; Lee and Neff, 2011; Røe Utvik, 1999).

Table 1
Toxicity to *Acartia tonsa* nauplii (48-hour lethality, given as 50 and 10% lethal concentrations) of PW total extracts (TOE) and 'polar/apolar' fractions, compared to measured TEM concentrations in PW effluents.

		PW concentration (mg L^{-1})	LC_{50} (mg L^{-1})	LC_{10} (mg L^{-1})
PW-A	TOE	8.0	0.44 (0.40–0.47)	0.082 (0.066–0.100)
	'Apolar'	3.3	0.87 (0.79–0.98)	0.109 (0.086–0.138)
	'Polar'	3.0	0.26 (0.23–0.30)	0.053 (0.039–0.073)
PW-B	TOE	17	0.052 (0.048–0.057)	0.013 (0.011–0.017)
	'Apolar'	6.0	0.052 (0.047–0.057)	0.023 (0.018–0.030)
	'Polar'	6.8	0.16 (0.15–0.18)	0.034 (0.027–0.043)
PW-C	TOE	68	0.34 (0.30–0.38)	0.057 (0.043–0.075)
	'Apolar'	14	*	0.079 (0.025–0.520)
	'Polar'	38	0.55 (0.49–0.63)	0.079 (0.057–0.109)
PW-D	TOE	28	0.89 (0.75–1.06)	0.071 (0.051–0.099)
	'Apolar'	19	*	0.79 (0.33–1.89)
	'Polar'	4.5	0.20 (0.19–0.21)	0.069 (0.062–0.076)
PW-E	TOE	14	1.7 (1.4–2.1)	1.00 (0.95–1.05)
	'Apolar'	4.8	1.1 (1.0–1.2)	0.36 (0.31–0.42)
	'Polar'	6.1	2.9 (2.2–3.8)	1.7 (1.7–1.8)

*Values too high to be determined. Values in parenthesis give 95% confidence intervals.

Qualitative GC × GC–MS of both non-derivatised (Fig. 4) and derivatised extracts provided greater chromatographic resolution than GC–MS. Analysis of the non-derivatised PW TOEs indicated compound classes such as BTEX (I), alkyl phenols and naphthalenes (II), saturated hydrocarbons (III) and alkyl phenanthrenes (IV), were common to all PW TOEs (Fig. 4). However, the profiles of the GC × GC–MS TIC chromatograms of the different TOEs differed in the relative abundances of each class. For example, the relative proportions of the volatile BTEX components were higher in the extracts of the PW-A, PW-B and PW-D, but lower in the PW-E and PW-C extracts (Fig. 4). It is important to note, however, that the relative distributions of the volatile PW components (e.g. BTEX) may have been affected by sample storage, transport and processing before the GC × GC–MS analysis.

GC × GC–MS of the same PW TOEs, but now derivatised with BSTFA, showed improved chromatographic behaviour for the more polar compounds in the extracts (e.g. Fig. S1) but the presence of residual derivatising reagent then resulted in masking of information on BTEX and compounds with similar volatilities, demonstrating the importance of applying multiple analysis modes to fuller characterization of such highly complex extracts.

The GC × GC–MS analyses of both underivatised (Fig. 4) and derivatised (e.g. Fig. S1) extracts produced large data sets which will require much more detailed study and manipulation in future to achieve a complete component characterization. However, mass spectral comparison and matching of the PW TOE components revealed by GC × GC–MS, with those of compounds registered in a NIST (v11) library, allowed tentative identification of some less commonly reported components in the different PW TOEs. The presence of these compounds in PW would be overlooked with any of the methods applied for routine monitoring.

Examples of such compounds identified in the TOE from PW-B analysed by GC × GC–MS included butoxyethoxy ethanol, 1,2,4-trithiolane and lenthionine. The former is a common PC (Kelland, 2009) whereas the latter two compounds are probably indicative of the use of H_2S scavenging chemicals during production (Kelland, 2009). In addition to the presence of butoxyethoxy ethanol in PW-C and PW-A TOEs, when derivatised (BSTFA) extracts were examined by GC × GC–MS they were also found to contain phenols and acyclic, alicyclic and aromatic carboxylic ('naphthenic') acids (NA) The derivatised PW-D extract contained observable traces of oil-derived hydrocarbons and benzoic acid, along with butoxyethoxy ethanol, carbazoles and amines (Fig. S1, some undoubtedly resulting from the use of PCs (Kelland, 2009)). Some of these were further confirmed by LC-MS, as follows.

Other, more polar and rarely (if ever) reported compounds originating from both the oil and from added PCs were revealed by the LC-MS analyses employed in the study. Here we show preliminary results using an untargeted approach to demonstrate the applicability of the LC-MS technique for the separation and detection of a wider range of polar compounds in PW that undoubtedly originate from PCs, oil and formation water.

The LC-MS data obtained were highly complex, however some conclusions on differences in composition and tentative identification of a few compound groups were possible. Comparison of the full scan LC-MS TIC chromatograms of the five PW TOEs (Fig. 5) showed significant differences in the overall profiles and comprised highly complex compositions, confirming and extending the results of analysis by GC × GC–MS. The observable differences in the TIC chromatogram profiles between the TOEs, would appear to be associated and attributable to different PCs used at each platform, stage of production and/or PW treatment at the time of sampling. An idea of the complexity of the LCRMS data was indicated with an initial evaluation of a trial version of the commercial software Compound Discoverer 3.0 (CD 3.0, Thermo Fisher Scientific, UK) which showed 60,000 to 100,000 potential compounds might be detectable in the five PW TOE samples. Such an inventory will require a major effort to identify, measure and validate which

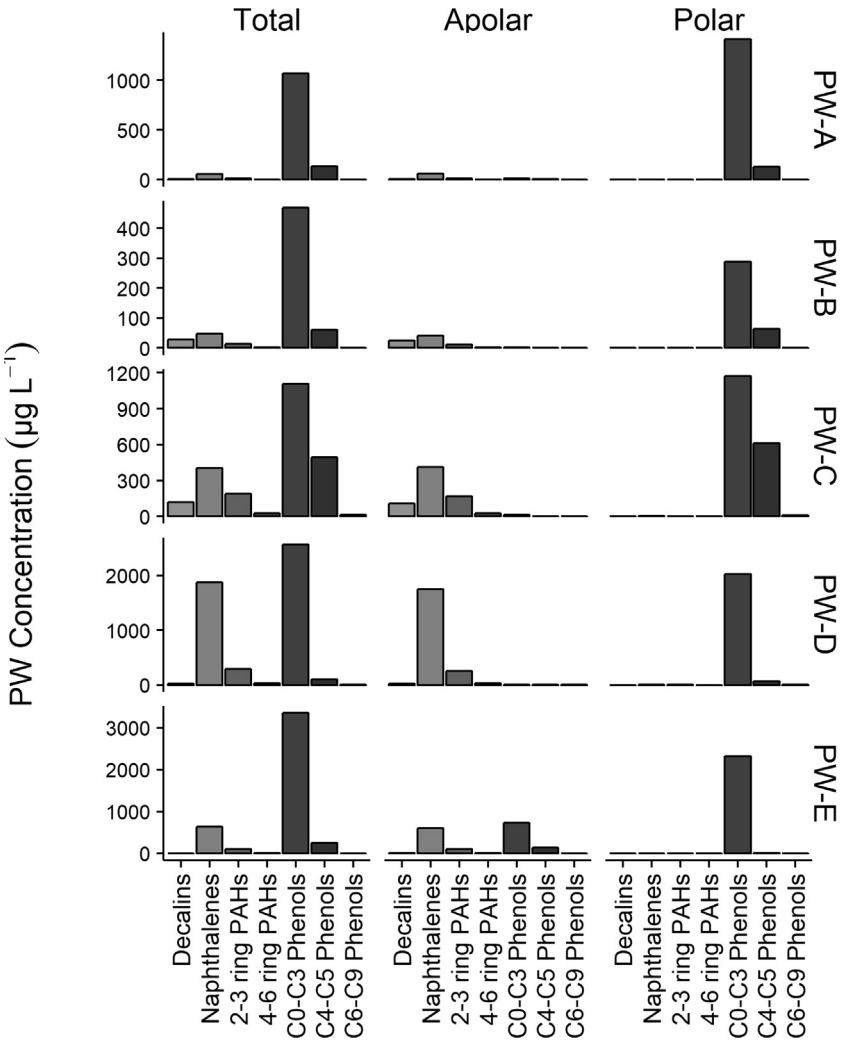

Fig. 3. Concentrations and profiles of decalins, PAHs and C0-C9 phenols in TOEs, 'apolar' fraction and 'polar' fraction of the five PWs. Different y-axes scales are displayed.

is beyond the scope of the current work (Further evaluation, application and optimisation of a purchased CD 3.0 is ongoing for related studies and will be reported as applicable). The following examples are illustrative of what could be determined using a manual approach.

High abundance peaks (RT 3.6 min) were observed in the TIC chromatograms of the extracts from the PW-A, PW-B and PW-C (Fig. 5). One of these produced a spectrum with an ion assigned to $[M + H]^+$ at *m/z* 163.13278 (Fig. S2, shown for PW-A). A predicted elemental formula $C_8H_{19}O_3$ ($[M + H]^+$, −0.55 ppm) was proposed by the software (FreeStyle). The experimental and simulated monoisotopic spectra compare well (Fig. S3). For a compound with molecular weight [M], a $C_8H_{18}O_3$ molecular formula is therefore suggested, for which a ChemSpider search (Royal Society of Chemistry, 2018a) produced 288 results. Of these, butoxyethoxy ethanol ($C_8H_{18}O_3$, also known as diethylene glycol, *n*-butyl ether (or DEGBE)) was also identified in the PW extract by GC–MS and GC × GC–MS. It was also noted (particularly) in the LC-MS data for the PW-C extract, that spectra with ions increasing by 44 Da were present. These are consistent with the presence of a series of butylpolyethoxylated compounds ($C_4H_9O(C_2H_4O)_nH$), (Fig. S4). Analysis of the exact mass EIC chromatograms (±5 ppm) for protonated $[M + H]^+$ butylpolyethoxylates ([M] = $C_8H_{18}O_3$, $C_{10}H_{22}O_4$, $C_{12}H_{26}O_5$, $C_{14}H_{30}O_6$, and $C_{16}H_{34}O_7$; Figs. S4–S8) show that for extracts of PW-C and PW-E PWs, $C_{10}H_{22}O_4$ (triethylene glycol butyl ether (TEGBE)) and $C_{12}H_{26}O_5$ (tetraethylene glycol butyl ether) were the more abundant compounds. Butylethoxylated based solvents, such as DEGBE and TEGBE, are widely used in oilfield PCs and indeed DEGBE was the major component observed in the PW-B TOE by positive ion LC-MS (TIC peak at RT 3.6 min, Fig. 5). A large number of polyethoxylated components are observed in all samples and will be the subject of further detailed interpretation and analyses.

For the PW-D TOE, two high abundance peaks were present at RT 8.08 and 9.66 min in the TIC chromatogram (Fig. 5) for which the mass spectra showed corresponding ions *m/z* 228.26849 and 256.29950 respectively (Figs. S9–S10), with no apparent adduct ions (due to NH_4, Na, or K) observable. The elemental formulae predicted by the software were: $C_{15}H_{34}N$ and $C_{17}H_{38}N$ (−0.36 and −1.47 ppm mass accuracies respectively) for which ChemSpider found nine and five quaternary amine-based compounds – so-called 'quats' (respectively (Royal Society of Chemistry, 2018b, 2018c)). 'Quats' are widely used in a wide range of PC products (Kelland, 2009). Alkyltrimethylammonium compounds are consistent with the formulae and exact mass EIC chromatograms for $[M]^+$ $C_{15}H_{34}N$, $C_{17}H_{38}N$ and the homologues $C_{19}H_{42}N$, and $C_{21}H_{46}N$ are shown in Fig. S11, corresponding tentatively to dodecyl, tetradecyl, hexadecyl and octadecyltrimethylammonium quats. The dodecyl and tetradecyltrimethylammonium components showed very high ion intensity responses at the limit of the MS instrument and peak tailing due to the high proportions of these two compounds relative to the longer chain hexadecyl and octadecyl homologues (Fig. S11) and other components in the sample. The other PWs did not contain these alkyldimethylammonium compounds at concentrations significantly greater than the DCM blank.

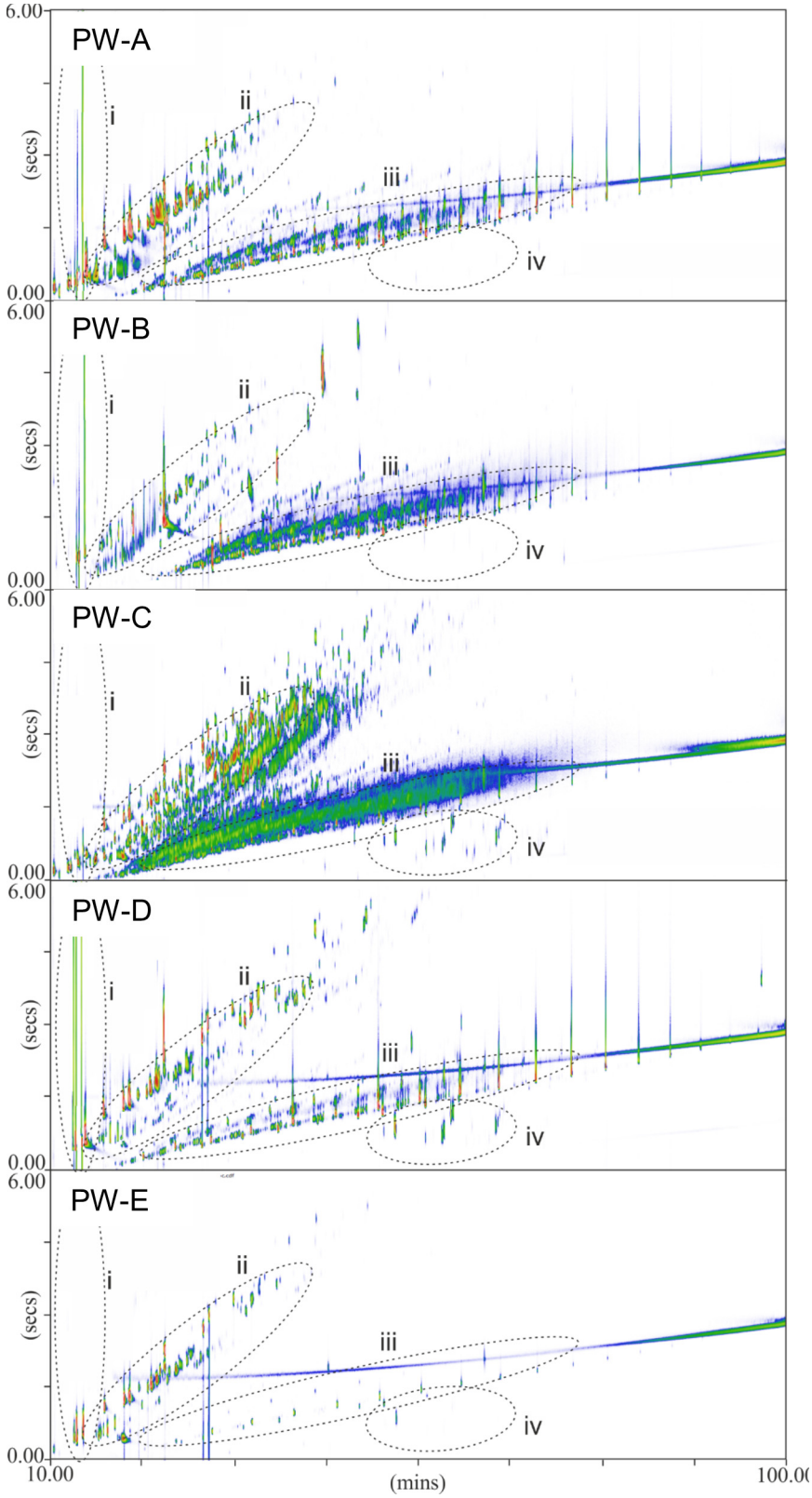

Fig. 4. GC × GC–MS TIC chromatograms of the non-derivatised TOEs from the five North Sea PWs. Highlighted on each chromatogram are areas in which various compound classes elute: i; BTEX, ii; alkyl phenols and naphthalenes, iii; saturated hydrocarbons, iv; alkyl phenanthrenes. Retention times are given in minutes in the first dimension (x-axis) and in seconds for the second dimension (y-axis).

Benzalkonium (alkyldimethylbenzylammonium quats) compounds have previously been shown to be components in PCs (McCormack et al., 2001). Peaks corresponding to these were observed in the PW-D TOE EIC chromatogram. For example, for dodecyl (RT 10.04 min, $C_{21}H_{38}N$), tetradecyl (RT 11.45 min, $C_{23}H_{42}N$), hexadecyl (RT 12.72 and 18.14 min, $C_{25}H_{46}N$), octadecyl (RT 13.88 and 19.99 min, $C_{27}H_{50}N$) and eicosanyl-dimethylbenzylammonium (RT 21.58 min, $C_{29}H_{54}N$) $[M]^+$ ions (Fig. S12). Two peaks where observed for each

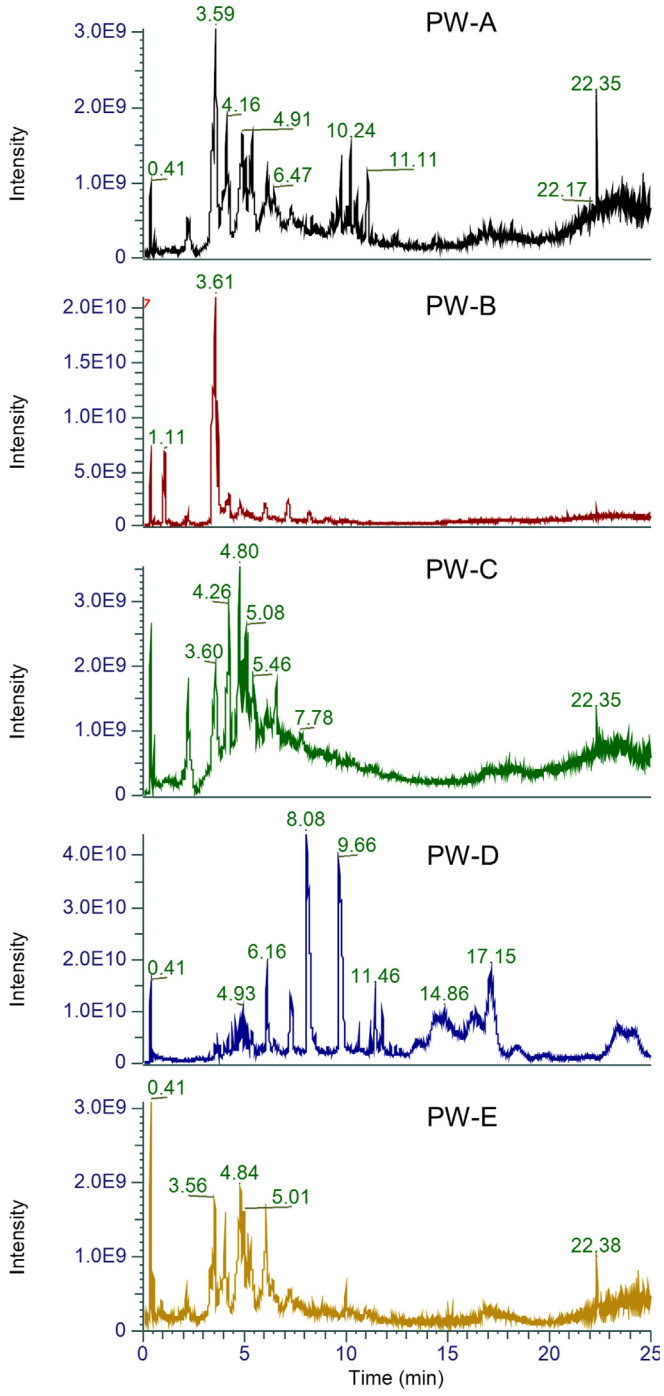

Fig. 5. LC-HRMS positive ion full scan MS *m/z* [100–1000] total ion chromatograms of the TOE of North Sea PWs (background subtracted).

$C_{25}H_{46}N$ and $C_{27}H_{50}N$ $[M]^+$ ion, suggesting different structures, which in this case were confirmed from the AIF-MS/MS data. It has previously been shown that ion trap collision induced dissociation (CID) MS^2 of benzalkonium precursor ions produce iminium product ions (McCormack et al., 2001) and that they would also be similar to the higher energy collision dissociation (HCD) MS/MS of the Quadrupole Orbitrap instrument used for these analyses. Indeed, AIF-MS/MS EIC chromatograms for iminium ion *m/z* (exact mass ± 5 ppm) $[M]^+$; $C_{14}H_{31}N$, $C_{16}H_{35}N$, $C_{18}H_{39}N$ and $C_{20}H_{43}N$, consistent with dodecyl, tetradecyl, hexadecyl and octadecyl-dimethylbenzylammonium quats (Fig. S13) were observed for the peaks at RT 10.04, 11.45, 12.72 and 13.88 min respectively (Fig. S12). The identity of the structural or functional isomer peaks at RT 18.14 min ($C_{25}H_{46}N$), 19.99 min ($C_{27}H_{50}N$) and 21.58 min ($C_{29}H_{54}N$) are unknown and were not observed in any other PW sample. The dodecyl and tetradecyl-dimethylbenzylammonium quats were the two most intense peaks with the hexadecyl and octadecyl-dimethylbenzylammonium quats <10% relative abundance in the PW-D EIC chromatogram (Fig. S12). The other PWs did not have ions significantly greater than the DCM blank for these alkyldimethylbenzylammonium compounds except dodecyl and tetradecyl-dimethylbenzylammonium quats in the PW-B TOE (Figs. S14–S15).

Imidazoline based compounds, such as the so-called 2:1 imidazolines are known components used as corrosion inhibitors and surfactants in PCs and are often produced as complex mixtures (McCormack et al., 2001, 2002). LC-MS spectra of PW-D and PW-A TOEs contained numerous ions likely associated with imidazolines. As an example, Figs. S16 and S17 (data for PW-D and PW-A) show the $[M + H]^+$ EIC chromatograms for the C_{18} fatty acid-derived 2:1 imidazolines with 0–6 double bonds. A ChemSpider search for $C_{40}H_{75}N_3O$ produced five suggested structures, all 2:1 imidazolines with the double bond in various positions on the alkyl chains (Royal Society of Chemistry, 2018d).

3.3. Understanding the influence of chemical composition on toxicity

The GC–MS, GC × GC–MS (e.g. Figs. 4 and S1) and LC-MS (Fig. 5) profiles of the five PW TOEs differed, as did the acute toxicities. PW-C was the PW with highest discharge content of total GC-amenable TEM compounds, followed by PW-D, PW-B and PW-E and finally, PW-A, with the lowest concentration. The PW-E had the second lowest concentration and the toxicity of the effluent was also less than observed for most other PWs.

On a mass basis, PW-B proved to be the most toxic PW, and PW-E the least toxic. Interestingly, the total GC-amenable TEM organics content in these two PWs was comparable, as were the proportions of 'polar' and 'apolar' GC-amenable TEM compounds. However, advanced chemical characterization revealed the presence of some PCs (e.g. trithiolane, lenthionine) in PW-B extract, which were not readily observed in any of the other PWs. It is therefore hypothesized that some PCs may also contribute to the toxicities of the PWs, but this cannot be confirmed based on the current study.

In this study, we demonstrate how PW toxicity cannot be solely attributed to the total release of PW, or to currently routinely measured compound groups. In Fig. 6 we propose a "risk chart" for PW, based on fractionation into so-called 'apolar' and 'polar' fractions, and comparison of toxicity (on a mass basis) of these fractions and the total PW. Level of toxicological concern increases from top left where fractions with high

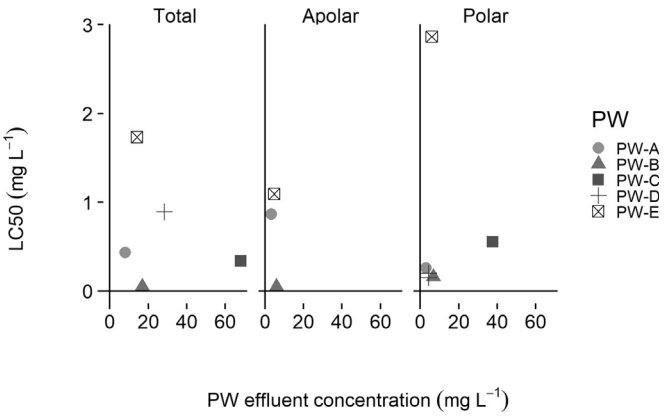

Fig. 6. LC_{50}-values and concentrations in mg L^{-1} of fractions from the five PWs identifies the fraction ('apolar' or 'polar') of most concern in each respective PC, by showing how the actual concentration of a fraction in PW effluent corresponds to the measured LC_{50}.

LC_{50} (low toxicity) combined with low concentration are found to low right where fractions with low LC_{50} (high toxicity) and high concentrations are found. This allows for convenience when determining where the toxicity for the total fraction comes from. As an example, the high LC_{50} and high concentration intersect of the PW-C TOE is also found in the polar fraction indicating that both the mass and the toxicity of that PW resides within the polar fraction. For any given PW, this chart might act as a guide as to which fraction should be investigated in more detail to try to explain the overall PW toxicity and to guide future monitoring of releases from the production platform. For instance, PW releases from the PW-E platform and PW-B platform should be monitored with focus on 'apolar' compounds (typically petrogenic compounds), while on the PW-C and PW-D platform, focus should be given to more polar contaminants. This might require a more thorough investigation of both polar and apolar organic compounds generally contributing to PW toxicity, following an approach similar to the one applied in the current study, and updating analytical protocols and monitoring guidelines to include these.

Components identified by GC × GC–MS analysis of the PW-B TOE (most toxic PW) included butoxyethoxy ethanol, trithiolane and lenthionine, the latter two probably related with the use of H_2S scavenging chemicals, whereas the PW-C and PW-A TOEs (intermediate toxicity) included phenols and acyclic, and alicyclic and aromatic carboxylic ('naphthenic') acids, in addition to butoxyethoxy ethanol. The PW-D extract (least toxic) contained observable traces of oil-derived hydrocarbons, along with butoxyethoxy ethanol and amines, but additional polar compounds deriving from both the crude oil and from added PCs were tentatively identified by LC-MS analysis, including polyethoxylates, 'quats' and imidazolines. Further research is needed to understand the contribution or non-contribution to toxicity of both PCs and less studied petrogenic compound groups present in PW.

4. Conclusions

The current study demonstrated the use of high-resolution analytical techniques in combination with toxicity testing to investigate the importance of potentially 'unknown' contributors to PW toxicity towards marine organisms. It was demonstrated that the acute toxicity of some PWs could be attributed mainly to components in an operationally-defined 'polar' fraction while the toxicity of other PW extracts was attributed mainly to the 'apolar' fractions. A range of previously uncharacterized PW 'polar' and 'apolar' constituents, including those likely derived from PCs, such as trithiolane, imadazolines and 'quats', were tentatively identified using advanced analytical techniques, including GC × GC–MS and LC-HRMS. This approach may suggest a way forward for future revisions of routine monitoring programs for operational discharges, being able to assist development of methods adequate to monitor the 'correct' compounds and compound groups from an ecological risk perspective.

CRediT authorship contribution statement

Lisbet Sørensen: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Data curation, Visualization, Investigation. **Paul McCormack:**Methodology, Formal analysis, Writing - review & editing, Data curation, Visualization, Investigation. **Dag Altin:**Methodology, Formal analysis, Resources, Writing - review & editing, Data curation, Visualization, Investigation. **William J. Robson:**Methodology, Data curation, Visualization, Investigation. **Andy M. Booth:**Conceptualization, Writing - original draft, Writing - review & editing. **Liv-Guri Faksness:**Conceptualization, Resources, Writing - review & editing, Visualization. **Steven J. Rowland:**Conceptualization, Methodology, Resources, Writing - original draft, Writing - review & editing, Data curation, Visualization, Supervision. **Trond R. Størseth:**Conceptualization, Formal analysis, Resources, Writing - original draft, Writing - review & editing, Data curation, Visualization, Project administration, Funding acquisition, Supervision.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.133682.

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