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1 Identification of Estrogen-Like Alkylphenols in Produced Water from Offshore Oil

2 Installations

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7 Abstract

8 Produced water released into the sea from oil installations contains a vast number of organic
9 compounds. This work focuses on the analysis and identification of phenols in produced
10 water, in particular long-chain *para*-substituted alkylphenols, which act as endocrine
11 disruptors for marine biota. Some alkylphenol standards, unavailable commercially, have
12 been synthesised and some compounds of interest identified. However, a complete
13 identification is not possible since conventional GC techniques cannot achieve the desired
14 degree of separation. An overview of the levels of the 52 known alkylphenols in produced
15 water from 9 oil installations in the North and Norwegian Seas has been made. The previously
16 unidentified alkylphenols in produced water have been characterised by means of alkylphenol
17 retention indices (APRI) and mass spectrometry, and their total amounts estimated for the
18 same 9 locations. Our results confirm the presence of naphthols and other as yet unidentified
19 compounds in produced water, while thiophenols were not detected by the used technique.

20 *Keywords:* Produced water; alkylphenols; endocrine disruptors; isomers; GC-MS; retention indices; APRI

21 1. Introduction

22 In oil exploration activities, produced water is the water that comes up with oil from sea bed
23 reservoirs, and is then separated from the oil and released into the marine environment. The
24 quantities are large ($147 \times 10^6 \text{ m}^3$ from Norwegian offshore oil activities in 2005) and ever
25 increasing due to a larger water content in maturing production wells. The cited 2005
26 releases are $4 \times 10^6 \text{ m}^3$ higher than those in 2004 (NPD, 2006). Total releases from all national
27 sectors throughout the North Sea are larger still, having reached $560 \times 10^6 \text{ m}^3$ already in 2002
28 (Thomas *et al.*, 2004a). The water released in the Norwegian sector each year contains tens of
29 thousands of tonnes of organic compounds, including hundreds of tonnes of alkylphenols
30 (OLF, 2006). Alkylphenols are potential endocrine disruptors, and are thus recognized as a

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31 matter of concern for marine biota (Nimrod and Benson, 1996; Meier *et al.*, 2007). Produced
32 water has been shown to contain estrogen receptor agonists, and alkylphenols have been
33 identified as major contributors to this effect (Thomas *et al.*, 2004a,b).

34 A sensitive and selective method for determination of alkylphenols in produced
35 water has recently been described (Boitsov *et al.*, 2004). The method is based on solid-phase
36 extraction with derivatisation by pentafluorobenzoyl chloride and gas chromatography-mass
37 spectrometry (GC-MS) analysis of the derivates using negative ion chemical ionisation, NCI.
38 The method has detection limits at low ng/l level and now uses 52 alkylphenols of different
39 chain length, from phenol (C₀) to nonylphenol (C₉), as standards. However, a large number of
40 alkylphenols are found in an average produced water sample. Theoretically, hundreds of
41 isomers may be present. Most of these are not commercially available and have not been
42 identified.

43 The primary aim of this work has been to help determine the endocrine-disrupting
44 potential of produced water, since only some alkylphenol isomers have been shown to exert
45 this effect. Namely, long-chain, branched (especially tertiary) *para*-substituted alkylphenols
46 have the strongest xenoestrogen effect, 4-*tert*-octylphenol being the most potent xenoestrogen
47 of all alkylphenols (Routledge and Sumpter, 1997). *Ortho*-substituted and short-chain
48 alkylphenols have little or no xenoestrogen effect (Routledge and Sumpter, 1997).

49 Here we describe the qualitative analysis of the total alkylphenol matrix in produced
50 water, together with the quantitative analysis of known alkylphenols in samples from various
51 Norwegian offshore oil installations. For the qualitative analysis, large sample volumes and
52 improved sample purification were used to achieve a high degree of analytical sensitivity and
53 selectivity for detecting as many alkylphenol isomers as possible. Several approaches were
54 then used to carry out identifications.

55 The first way to identify the unknown chromatographic peaks is to synthesise some
56 of the alkylphenol isomers that are not currently available commercially. Having synthesised
57 a few tertiary *para*-substituted long-chained alkylphenols, it may be possible to determine a
58 significant part of xenoestrogens in produced water. However, this leaves the rest of the
59 alkylphenol matrix unidentified.

60 Identification of alkylphenols in produced water may be facilitated by mapping all
61 the unidentified isomers to provide a reliable basis for the analysis of hundreds of compounds
62 for which standards do not exist. An efficient way of achieving such systematisation is by
63 using retention indices. The retention index is the retention time of the analysed compound
64 expressed relative to the retention times of a series of reference compounds. A method of

alkylphenol retention indices (APRI) has been developed and applied to alkylphenols in produced water (Mjøs *et al.*, 2006). It has been shown to be more robust for this purpose than the traditionally used Kovats indices, and allows accurate characterisation of alkylphenol isomers despite changes in chromatographic properties such as retention times. Thus, a systematisation of separate alkylphenol isomers becomes possible, resulting in unequivocal determination of any given alkylphenol isomer in various samples analysed under various chromatographic conditions, without the use of standards.

In addition to alkylphenols, thiophenols and naphthols have also been included in the analysis. These compounds have not previously been studied in produced water; however, their presence in oil has been shown (Beens and Tijssen, 1997; Thomson *et al.*, 1997) and their toxicity towards bacteria or higher marine organisms investigated (Londry and Suflita, 1998; Falk-Petersen *et al.*, 1985; Cajaraville *et al.*, 1989). These two classes of compounds can undergo pentafluorobenzoyl derivatisation (Thomson *et al.*, 1997) and may therefore be analysed by the same procedure as the one used for alkylphenols.

2. Materials and Methods

2.1. Sampling strategy

Large volumes (100 l) of produced water samples have been used to provide sufficient concentrations for analysing even the minor compounds. This was necessary, since many alkylphenols, particularly long-chain ones, are found only in small quantities in produced water. This study was not quantitative due to the novelty of the task, the absence of standards for establishing response factors, and because of the complicated multi-step procedure. However, smaller volumes of samples originating from 9 oil installations in the North and Norwegian Seas have been analysed for levels of the known alkylphenols by a previously described quantitative procedure (Boitsov *et al.*, 2004), and the amounts of the unknown isomers have also been estimated. All together, the following 13 samples of produced water from 10 oil installations (see Fig. 1) in the Norwegian sector of the North Sea and the Norwegian Sea have been analysed in this work:

1. 2 large-volume (100 l) samples from Statfjord A and Statfjord B oil installations (sampled on January 28 and 29, 2005), to be used for qualitative analysis of even minute concentrations of unknown alkylphenols;

2. 9 regular volume (100 ml) samples from all oil installations except Statfjord B (sampled on various dates in August 2005), to be used for quantitative analysis of known alkylphenols;

3. 2 regular volume (100 ml) samples from Statfjord C and Oseberg C oil installations, without HCl added (sampled in August 2005, simultaneously with the samples to which HCl was added), to be used for checking the efficiency of the conservation procedure.

A blank sample of 100 ml distilled water has been analysed together with regular volume samples for quantitative analysis purposes. All samples except the ones mentioned in point 3 above were added 1% vol. of HCl:water 1:1 mixture for conservation immediately upon sample collection. After that, the samples were sent without airing to the laboratory and stored for 1 to 3 weeks at +2°C in the dark until analysis.

(Figure 1)

2.2. Chemicals and syntheses

2.2.1. Chemicals

Pure standards (95-99.9%) of 49 alkylphenols and 5 deuterated alkylphenols, 3 thiophenols and 2-naphthol were from Sigma-Aldrich (Oslo, Norway) and Chiron (Trondheim, Norway). Standard solutions were prepared in methanol. The derivatisation agent, pentafluorobenzoyl chloride (PFBC) was from Sigma-Aldrich. Solvents (methanol, hexane, *tert*-butyl-methyl ether, formic acid, toluene, isopropanol) were analytical grade from Merck (Oslo, Norway) and Arcus (Vestby, Norway). Sodium hydroxide (NaOH), sodium bicarbonate (NaHCO₃) and hydrochloric acid (HCl) were from Merck. Alcohols and alkenes used for syntheses were from Sigma-Aldrich (Oslo, Norway) and Alfa Aesar (Karlsruhe, Germany). The catalysts used for syntheses, AlCl₃ and Amberlite IR-112 resin, were from Sigma-Aldrich (Oslo, Norway). The distilled water used was purified with NANOPURE Ultrapure Water Systems (USA). Solid-phase extraction Oasis® cartridges with anion-exchange MAX sorbent were from Waters (Milford, MA, USA).

2.2.2. Syntheses

The general procedure for the synthesis of *para*-substituted alkylphenols is well known, involving Friedel-Crafts reaction and certain catalytic and/or physical conditions to achieve

the desired selectivity. Syntheses of long-chain tertiary alkylphenols have been carried out at the University of Bergen according to the two following procedures. An acid-catalysed reaction between phenol and substituted alcohols leads to pure single isomer products (Huston and Hsieh, 1936); another one with phenol and an isoalkene as substrates and an ion-exchange resin as catalyst yields a mixture of the corresponding *ortho*- or *para*-alkylphenol isomers (Loev and Massengale, 1957). The first procedure was used for specific syntheses of 3 *para-tert*-alkylphenols and the second one for non-specific syntheses of mixtures of various tertiary alkylphenol isomers. Products were recrystallised consecutively from pure dichloromethane and a hexane-dichloromethane 3:1 mixture and dried in oil vacuum (in case of solid product), or the solvent was removed by rotor vapour (in case of liquid product). Products were then analysed by GC-MS (full scan) and by 400 MHz ^1H nuclear magnetic resonance (NMR) with deuteriochloroform (CDCl_3) used as NMR solvent and reference. Only pure products were analysed by NMR since NMR spectra of the mixtures could not be resolved. The products of the syntheses are described in Table 1.

(Table 1)

2.3. Extraction and purification

The 100 ml samples were purified by filtration and solid-phase extraction, with subsequent derivatisation by pentafluorobenzoyl chloride, according to the procedure described previously (Boitsov *et al.*, 2004). A method blank, made in distilled water, was processed together with the produced water samples. Quantitative data obtained for the produced water samples has then been corrected for blank values. The following detailed description of the experimental procedure concerns only the 100 l samples.

In this work we improved our regular purification procedure by introducing two extra steps, gel-permeation chromatography (GPC) and normal-phase liquid chromatography (NP-LC). GPC was used to remove small molecules like elementary sulphur and large polymer compounds that could interfere with the analysis. The following NP-LC step prevents an overlap of the signals from alkylphenols with those from other compounds (Snyder *et al.*, 2001). All alkylphenols were found in the same NP-LC fraction, well separated from PAH and other compounds. Samples were then sufficiently clean to provide MS spectra of good quality.

Each of the 100 l samples was first extracted with 2x50 ml dichloromethane (DCM) for every 2 l water, the extract volume was then reduced to approximately 0.5 ml under gentle

nitrogen gas flow in a water bath at 40° C. The extracts were mixed together and the volume was again reduced to approximately 5 ml. The two resulting extracts were then filtered, the filters washed with DCM and the filtrates extracted with acetonitrile-hexane, and the polar fraction was further fractionated by GPC, with the solvent exchanged to DCM. Both DCM and acetonitrile-hexane extraction efficiency was checked by analysing standard solutions of alkylphenols extracted in a similar way, achieving recoveries usual for this method (Boitsov *et al.*, 2004).

2.3.1. GPC

Gel permeation chromatography (GPC) was used for the 100 l samples to remove sulphur and other interfering compounds. The GPC cleanup was performed using systems from Gilson (Gilson 232 autoinjector, injector Gilson 401 dilutor, Gilson 202 fraction collector, Gilson, France) and Pharmacia (LKB 2150 HPLC pump, LKB 2252 LC controller, LKB 2144 fluorescence detector, Pharmacia LKB, Sweden). Two GPC columns from Waters (Envirogel GPC cleanup 19 mm x 300 mm) were used, coupled together using Gilson 232 autoinjector as a switch vent. The setup and cleanup procedure are described in more detail elsewhere (Meier *et al.*, 2005). The elution was performed with DCM at a flow rate of 5 ml/min. Samples were subjected to GPC twice and the resulting purity of the alkylphenol fraction was confirmed by GC-FID.

2.3.2. NP-LC

After GPC cleanup, the solvent was exchanged to hexane and samples were subjected to NP-LC cleanup and fractionation. For this, the same Gilson fractioning system and Pharmacia fluorescence detector as for GPC was used, but the NP-LC pump was from Shimadzu (LC-9A with FCV-9AL low-pressure solvent mixer). The NP-LC column (150x4.6mm, LiChrosorb 60-5 Si) was from Varian (Middelburg, the Netherlands). Injection volume was 500 µl at a time. A gradient of 0 to 6% isopropanol in hexane was used as mobile phase. Fractions of 4 ml were collected from 0 to 30 min.

15 fractions were obtained, with alkylphenols being concentrated in fraction 8 (from 14 to 16 min), up to 97% according to GC-FID measurements. Other polar compounds eluted in fractions 4-15, while PAH and other non-polar hydrocarbons eluted in fractions 1-3. All the NP-LC fractions were then derivatised by pentafluorobenzoyl chloride as described previously (Boitsov *et al.*, 2004). 2 compounds in fraction 8 have been identified as belonging to the naphthol class, one of them being 2-naphthol.

2.4. GC-MS analysis

All analyses were performed on an Agilent 6890 GC system connected to an Agilent 5973 mass selective detector with either electron impact (EI) ionization, or negative chemical ionisation (NCI), in full scan mode, scanning from m/z 50 to 500, or in selected ion monitoring (SIM) mode.

Samples of 0.1 l were analysed in NCI SIM mode according to the quantitative procedure described earlier (Boitsov *et al.*, 2004), routinely used for this purpose at our laboratory. The following deuterated internal standards were used for quantification: phenol- d_5 , as reference for phenol; cresol- d_8 , as reference for cresols; 4-ethylphenol- d_8 , as reference for C_2 -alkylphenols; 4-propylphenol- d_{12} , as reference for C_3 - C_6 alkylphenols; 4-nonylphenol- d_4 , as reference for C_7 - C_9 alkylphenols.

Samples of 100 l were analysed non-quantitatively by both EI and NCI, both in SIM and full scan mode, as described below. The analyses of the EI mass spectra yield structure information while the NCI spectra lead to improved sensitivity and selectivity.

A Varian Factor Four VF-5ms (Varian, Lake Forest, CA, USA), $L = 50$ m, I.D. = 0.25 mm, $df = 0.25$ μ m, was used as analytical column. Helium (99.9%) was used as carrier gas in 22 cm/s constant flow mode. The samples (1 μ l hexane solution) were injected in splitless mode and the split valve was opened after 2 min. The GC program was optimised for alkylphenol analyses as described by Mjøs *et al.* (2006). The oven temperature was 60°C at injection. After 2 min the temperature was increased to 100°C by a temperature programming rate of 30°C/min, which was followed by a second rate of 2°C/min to a final temperature of 260°C. Dwell time per ion for all ions was 100 ms. In SIM mode, the total chromatogram was divided into 5 windows (after solvent delay, 10 min), each of these scanned for 4 to 5 selected ions to achieve better sensitivity. The corresponding parameters are shown in Table 2.

(Table 2)

For naphthol analysis, the derivatised NP-LC fractions have been scanned in NCI mode for ion mass 338, corresponding to pentafluorobenzoyl derivates of C_1 -naphthols, and analysed in EI mode. 2-naphthol was used as a standard for determining compounds of naphthol type in produced water.

For thiophenol analysis, the derivatised NP-LC fractions have been scanned in NCI mode for ion masses 318, 332, 346, 360, 374, 388, 402 and 416, corresponding to

pentafluorobenzoyl derivatives of C₁-C₈ thiophenols, and analysed in EI mode. 4-Thiocresol, 4-ethylthiophenol and 3,4-dimethylthiophenol were used as standards.

3. Results and discussion

3.1. Qualitative analysis: large-volume samples.

3.1.1. Alkylphenols.

A large number of alkylphenol isomers is present in produced water, only a portion of which are identifiable from available standards (see Fig. 2). The number of non-identified alkylphenols grows rapidly with alkyl chain length, as shown in Table 3.

(Figure 2)

(Table 3)

Here we have employed a variety of methods in an attempt to characterize the unidentified alkylphenols. Large produced water samples (100 l) from Statfjord A and Statfjord B platforms were used for the detailed, non-quantitative investigations described below. More than 350 compounds have been definitely or tentatively identified as alkylphenols with up to 8 carbon atoms in the alkyl substituents, by means of visual investigation of mass spectra. Of these, 305 peaks belonged to unidentified alkylphenols, which is apparent from m/z 195 (EI) belonging to the pentafluorobenzoate fragment, and the corresponding molecular peak for each alkylphenol; the rest were identified by means of the available standard.

The alkylphenol retention indices, APRI, developed for this work (Mjøs *et al.*, 2006), have been used to systematise all the detected alkylphenols. APRI can be calculated by the following equation (1):

$$APRI_x = n \frac{t_{R(x)} - t_{R(z)}}{t_{R(z+n)} - t_{R(z)}} + z \quad (1)$$

where t_R is retention times of the compound of interest, x , and two *para*-substituted n -alkylphenols eluting on each side of the compound. z represents the number of carbon atoms in the alkyl chains of the *para*-alkylphenols eluting before x , and n is the difference in the number of carbon atoms between the two references. z is zero if the first reference compound is phenol.

This systematisation provides a standard list of alkylphenols found in produced water, each compound on this list being assigned a unique number in accordance to its APRI value. Even though the precise isomeric structure of each particular compound remains unknown, this allows a determination of the same compound in any new sample on a similar stationary phase (for details, see Mjøs *et al.* (2006)). A selection of unidentified alkylphenols systematised in this way is shown in Section 3.2.

The biggest problem when attempting to identify the previously unidentified long-chain alkylphenol isomers in produced water was the poor resolution of the peaks, despite the optimised GC conditions. Obviously, conventional GC-MS techniques do not provide sufficient data quality for this type of analysis, and supplementary or different techniques have to be used to achieve complete peak separation. In recent years, there have been substantial achievements in the development of methods for the mathematical resolution of overlapping chromatographic peaks (De Juan and Tauler, 2003). Most of these methods are multivariate procedures that reconstruct both chromatograms and spectra of the overlapping chromatographic peaks (Liang *et al.*, 1993). It has been shown that with the proper selection of instrument parameters and pretreatment of data, it is possible to resolve overlapping peaks with very similar spectra (Mjøs, 2003). However, this is a rather time-consuming procedure when complex matrices such as produced water are studied, in which hundreds of peaks need to be resolved. An alternative solution to the problem is the use of a two-dimensional separation technique. Among these, GCxGC seems to be the most efficient technique that is suitable for analysis of complex samples (Dallüge *et al.*, 2003). Thus, 40 isomers of 4-nonylphenol present in technical nonylphenol mixture have been successfully separated by GCxGC coupled to time-of-flight mass spectrometer, although precise structural elucidation remained impossible since the samples were not derivatised (Moeder *et al.*, 2006).

The mixtures of (*ortho*-, *para*-)hexyl- and heptylphenols were synthesised to determine xenoestrogenic *para*-isomers of long-chained alkylphenols in produced water and compare their relative amount to that of their less potent *ortho*- and *meta*-isomers. It has been observed for technical nonylphenol, representing a mixture of known nonylphenol isomers (Ruß *et al.*, 2005), when derivatised with PFBC and analysed together with other standards, that the majority of *para*-isomers have APRI values in the range of 7.1 to 7.7, eluting in a narrow chromatographic “window” as a cluster of peaks. These are strongly branched alkylphenols, while *para-n*-nonylphenol has APRI=9. Therefore, we expected the *para*-isomers in the synthesised mixtures to elute closely together as well. However, their APRI values were found to span a wide range, unlike those of technical nonylphenol, and the

samples therefore did not provide a basis for identification of clusters of *para*-substituted hexyl- or heptylphenols.

3.1.2. Thiophenols.

No compounds of thiophenol class have been found in the studied samples. The absence of thiophenols could be partly due to the pre-analysis sample preparation procedure that was not optimised for this type of compounds. However, the large volume of the analysed samples, 1000 times larger than the regular volume used for routine analysis of produced water at our laboratory, allows to suggest that the amounts of thiophenols in produced water are insignificant.

3.1.3. Naphthols.

Two compounds in the studied samples have been identified as belonging to the naphthol class (C₁-naphthols, derivate molecular mass 338), one of them identified as 2-naphthol by means of the used standard. Qualitative results suggest that the concentrations of naphthol are rather limited, possibly 10 to 50 times smaller than the concentrations of alkylphenols of similar mass (C₃-alkylphenols, derivate molecular mass 330), i.e. at µg/l or below.

3.1.4. Other compounds.

A large number of unidentified compounds with molecular masses 328, 342, 356, 370 and 384 have been determined in the produced water samples. The same type of compounds have previously been observed in produced water from the Oseberg C oil installation (Boitsov *et al.*, unpublished results). The masses differ by 2 from C₃-C₇ alkylphenol pentafluorobenzoates; however, the relative amounts of the compounds are comparable to or even larger than those of the corresponding alkylphenols (Fig. 3). Similar compounds with masses differing by 4 from masses of alkylphenol derivatives have also been observed.

(Figure 3)

A similarity between the mass spectra and chromatographic parameters of these compounds and those of alkylphenol derivatives has given rise to a suggestion that the unknown compounds may be alkylphenols with unsaturated alkyl chains, *i.e.* alkenylphenols and alkynylphenols. Alkenylphenols are known to exist in nature, for instance in certain tropical plants (*e.g.*, gibbilibols, compounds with cytotoxic and antibacterial properties (Orjala *et al.*, 1998)) and

are also known to be formed as by-products during the photodegradation of alkylphenols or alkylation of phenol (Kohtani *et al.*, 2005; Brodskii *et al.*, 1973). Confirming the identity of the unknown compounds still remains to be done.

3.2. Quantitative analysis: regular volume samples.

Forty-nine alkylphenols have been identified and quantified in 100 ml produced water samples from 9 oil platforms by means of commercially available alkylphenol standards or by those synthesised in our laboratory. It is worth pointing out that the previously described analytical method used in this study (Boitsov *et al.*, 2004) allows for more precise measurements than some other commonly used methods not involving derivatisation of analytes, such as the one recommended to oil companies by the Norwegian Oil Industry Association (OLF) (OLF, 2003). The results presented below are thus different from those reported by Norwegian oil companies or by studies that use the OLF-endorsed method, which may result in a considerable underestimation of short-chain alkylphenol levels and an overestimation of long-chain alkylphenol levels (*e.g.*, OLF, 2006).

The results from our study are given in Table 4, with APRI values given for each alkylphenol. The amounts of alkylphenols in the samples vary significantly from platform to platform, up to 3 orders of magnitude in some cases, thus reflecting a strong dependence of produced water composition on the origin of the oil. The difference in concentrations of long-chained alkylphenols is, however, much smaller than that of phenol and short-chained alkylphenols, indicating that the endocrine-disrupting ability of produced water does not change as much from platform to platform as the overall toxicity.

(Table 4)

The main results of this study include a description of the levels of tertiary *para*-alkylphenols, the most potent xenoestrogens found in produced water. Significantly, the 3 tertiary *para*-alkylphenols, synthesised in the course of this work, 4-(1,1-dimethylbutyl)phenol, 4-(1,2,2-trimethylpropyl)phenol and 4-(1,1-dimethylpentyl)phenol have all been identified in produced water. The quantity of these compounds seemed to be relatively low, when compared to other alkylphenols of similar alkyl chain length. The total amount of the eight quantified *para-tert*-alkylphenols does not exceed 1.75 µg/l in any sample and is, as expected, heavily dominated by the least potent, but the most water-soluble compound, 4-*tert*-butylphenol. The largest amounts of the 8 xenoestrogens were found in

discharges from Statfjord A, Statfjord C and Oseberg C platforms (see Table 4), which remains true even if 4-*tert*-butylphenol is not taken into account. A recent bioassay study of produced water from the same 10 platforms has also found samples from these 3 platforms to have the highest xenoestrogen potency, up to an equivalent of 4.0 ng/l 17- β -estradiol (Tollefsen *et al.*, 2007). This points to the crucial role that alkylphenols play in xenoestrogen potency of produced water.

Earlier *in vitro* screening of produced water samples from the UK sector of the North Sea has revealed even higher estrogen equivalents, up to 91 ng/l 17- β -estradiol for some samples (Thomas *et al.*, 2004a). This significant xenoestrogen potency of produced water has a clear endocrine-disrupting effect on marine biota like codfish (Meier *et al.*, 2007); however, upon release into the sea and consequent rapid dilution, the effect disappears. A risk assessment modelling study has predicted no effect on codfish except in close proximity of the discharge points (Myhre *et al.*, 2004); this has now been confirmed both by *in vivo* experiments (Meier *et al.*, 2007) and field experiments studying codfish caged near the discharge sites (Børseth and Tollefsen, 2004; Scott *et al.*, 2006). The field experiments have shown a weak induction of estrogen biomarker, vitellogenin, in the fish from cages put closest to the oil platform, within 500 m from the point of discharge (Scott *et al.*, 2006). Current work reported no alkylphenols found in liver of wild North Sea codfish (Grøsvik *et al.*, 2007).

Samples from two of the oil platforms, Statfjord C and Oseberg C, were tested for stability when the conservation agent, HCl, was not added. Two separate samples, one with and one without HCl, were obtained from each platform. No significant differences in the concentrations were observed between the two samples in either case, except some for *ortho*-substituted alkylphenols, due to the lowered efficiency of the method for these compounds (Boitsov *et al.*, 2004). This confirms the reliability of analysis, which is best suited for *meta*- and *para*-substituted alkylphenols. Thus, alkylphenols in produced water seem to be stable towards bacterial or other degradation when kept cool and in darkness in tightly sealed glass bottles for up to 3 weeks.

The 4-nonylphenol that was found in some, but not all, samples in quantifiable amounts (see Table 4) is thought to originate from sources other than produced water, due to the omnipresence of nonylphenols in the laboratory environment (Meier *et al.*, 2005).

An estimate of the amounts of unidentified alkylphenols has also been made for the nine 100-ml samples. The established APRI system provided a confirmation of the presence of the same compounds in different samples for all the unknown alkylphenols. However, since these compounds are not available as standards, it was not possible to establish response

factors for them, so a response factor of 1 was used. This cannot be regarded as an absolute quantification; however, it may be helpful to give a rough estimate of the amount of the compound present, and especially to compare relative amounts between produced water samples from different locations. The total amounts for each molecular mass are shown in Table 4, while concentration estimates for the selected separate unknown alkylphenols (given as an average for the 9 locations) are shown in Table 5. All the unidentified C3-alkylphenols are shown. For other alkylphenols, due to the large number of peaks (see Table 3), only two of each are shown: those which, on average, appear in the largest amounts in the samples.

(Table 5)

4. Conclusion

In this work, an attempt has been made to investigate the previously unidentified alkylphenols in produced water released into the sea from offshore oil installations. Two 100 l samples from 2 locations in the North Sea have been used for a detailed qualitative analysis. Three alkylphenols of high xenoestrogenic power were synthesised and identified in produced water. A system of alkylphenol retention indices, APRI, developed for this work, has been used to systematise all the observed alkylphenols, including the numerous unidentified ones. This may facilitate further work to identify the unknown isomers. However, poor peak separation precludes such analysis from being comprehensive, and other separation techniques, such as GCxGC, are likely to be necessary. Other compounds, such as naphthols, were also found in the samples, while thiophenols were not observed.

We also determined the concentrations of 52 alkylphenols found in produced water from 9 offshore platforms in the North and Norwegian Seas, including the three newly synthesised ones. While the levels of low-weight alkylphenols vary greatly from location to location, only moderate differences have been observed in the levels of long-chained alkylphenols. The results seem to support recent biological *in vivo*, *in vitro*, and field study data in their conclusion that estrogenically induced endocrine-disruption in the marine biota, due to produced water discharges, is only probable in the immediate vicinity of the point of discharge.

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Figure captions

Figure 1. The map of oil installations used for produced water sampling.

Figure 2. Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion chromatograms of a standard solution of known alkylphenols (a) as compared to produced water samples (b) for ion masses 330 (C3-alkylphenols), 344 (C4-alkylphenols) and 358 (C5-alkylphenols).

Figure 3. Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion chromatograms of derivatised produced water sample from Statfjord B oil platform, for two ion masses. Ion 358: C7-alkylphenol derivatives. Ion 356: the unknown compounds.

578 Table 1. A description of the products of the syntheses.

Type of product	Main product	Description	¹ H NMR chemical shifts, ppm
Pure C ₆ -alkylphenol	<i>4-(1,1-dimethylbutyl)phenol</i> .	Black-green oily liquid.	0.80-0.87 (t), 1.04-1.15 (m), 1.27 (s), 1.52-1.58 (m), 3.98 (s), 6.76-6.81 (d), 7.18-7.24 (d).
Pure C ₆ -alkylphenol	<i>4-(1-methyl-2,2-dimethylpropyl)phenol</i> .	Yellow crystals.	0.73-0.78 (d), 1.22 (s), 1.81-1.89 (m), 3.99 (s), 6.73-6.80 (d), 7.16-7.23 (d).
Pure C ₇ -alkylphenol	<i>4-(1,1-dimethylpentyl)phenol</i> .	Black oily liquid.	0.80-0.87 (t), 0.99-1.08 (m), 1.17-1.25 (m, unres.) 1.27 (s), 1.52-1.60 (m), 3.98 (s), 6.74-6.80 (d), 7.17-7.23 (d).
Mixture of (<i>ortho</i> -, <i>para</i> -)hexylphenols	<i>4-(1-methyl-2,2-dimethylpropyl)phenol</i> .	Clear colourless liquid.	-
Mixture of (<i>ortho</i> -, <i>para</i> -)hexylphenols	<i>4-(1,1-dimethylbutyl)phenol</i> .	Clear red liquid.	-
Mixture of (<i>ortho</i> -, <i>para</i> -)heptylphenols	<i>4-(1-methyl-3,3-dimethylbutyl)phenol</i> .	Clear pink liquid.	-

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Table 2. Selected ion monitoring (SIM) mode parameters used for alkylphenol analysis.

No.	Ion masses	Cycles/second
1	288, 293*, 302, 309*, 316	1,91
2	316, 325*, 330, 341*, 344	1,91
3	330, 341*, 344, 358	2,37
4	330, 344, 358, 372, 386	1,91
5	372, 386, 400, 414, 418*	1,91

* - Ion masses of deuterated alkylphenols used as internal standards.

Table 3. Number of alkylphenol peaks in GC-MS chromatograms of produced water samples.

<i>Alkylphenol chain length</i>	<i>Alkylphenol derivate mass</i>	<i>Identified alkylphenol peaks</i>	<i>Non-identified alkylphenol peaks</i>	<i>Total</i>	<i>Of them clusters</i>	<i>Theoretically possible</i>
<i>C0</i>	288	1	0	1	0	1
<i>C1</i>	302	3	0	3	0	3
<i>C2</i>	316	9	0	9	1	9
<i>C3</i>	330	11	9	20	3	21
<i>C4</i>	344	9	35	44	6	59
<i>C5</i>	358	6	45	51	14	143
<i>C6</i>	372	5	93	98	45	370
<i>C7</i>	386	3	88	91	18	936
<i>C8</i>	400	2	35	37	21	2287
<i>Total</i>		49	305	354	108	3829

Table 4. Concentrations of alkylphenols (with their APRI values) in produced water from 9 oil platforms in the North and Norwegian Seas, µg/l (*nq* – not quantifiable, *i.e.* peaks below the limits of quantification; *nd* – not detected, *i.e.* peaks below the limits of detection). *Para*-substituted tertiary alkylphenols are shown in italics. For limits of detection and quantification, and the method uncertainties, see Boitsov *et al.* (2004).

Oil installations												
Compound	APRI	Troll B		Statfjord		Åsgard B	Grane	Oseberg		Gullfaks		Oseberg
		A	C	C	Heidrun			Snorre A	B	C*		
Phenol	0.0000	18.9	2033.2	2426.1	20228.8	325.7	8748.8	2060.7	2126.8	272.9	2468.4	8227.2
C1-alkylphenols												
o-Cresol	0.6847	7.9	861.2	658.8	5402.0	164.6	2954.8	297.4	1026.3	285.5	1267.4	3984.1
m-Cresol	0.8990	11.5	1034.9	1011.5	4073.3	142.8	3667.1	317.6	818.5	232.8	1136.9	3735.9
p-Cresol	1.0000	10.2	1187.3	1102.2	4264.8	55.0	2553.3	861.4	466.1	330.4	1064.9	2534.4
Sum total C1-alkylphenols		29.6	3083.3	2772.5	13740.2	362.4	9175.2	1476.4	2310.9	848.7	3469.2	10254.4
C2-alkylphenols												
2-Ethylphenol	1.3203	0.58	22.37	16.92	62.69	2.39	45.13	14.14	10.18	11.31	27.70	49.76
2,6-Dimethylphenol	1.4847	6.08	48.62	27.26	68.84	11.64	86.60	9.62	43.38	14.24	76.51	147.54
2,5-Dimethylphenol	1.6379	18.06	99.81	70.32	79.96	10.87	154.76	26.49	40.74	22.03	100.54	160.62
2,4-Dimethylphenol	1.7354	21.59	143.14	102.69	133.08	6.33	198.76	40.26	29.66	64.01	115.48	191.19
3-Ethylphenol	1.7772	20.52	61.49	61.42	167.09	5.35	156.52	39.88	21.80	49.57	79.97	159.79
3,5-Dimethylphenol	1.8774	37.52	79.86	63.89	149.48	7.30	167.62	24.45	35.12	24.68	66.30	164.73
4-Ethylphenol	2.0000	9.03	42.08	30.67	63.99	6.13	61.74	35.36	17.40	23.21	39.59	72.89
2,3-Dimethylphenol	2.0214	6.82	28.80	29.17	59.71	4.85	49.46	28.44	14.67	17.14	35.79	56.01
3,4-Dimethylphenol	2.3089	5.91	63.23	55.86	50.37	3.80	96.62	30.43	19.30	24.26	50.20	96.17
Sum total C2-alkylphenols		126.11	589.41	458.20	835.21	58.66	1017.23	249.06	232.26	250.45	592.10	1098.70
C3-alkylphenols												
2-Isopropylphenol	1.6379	2.39	13.56	11.54	2.34	0.48	9.75	1.74	3.45	2.46	11.62	10.05
2-n-Propylphenol	2.0550	0.25	2.48	2.13	6.50	0.11	3.88	0.75	1.12	0.51	2.31	3.99
3-Isopropylphenol	2.2813	7.85	15.18	11.96	15.85	0.84	21.42	3.40	2.45	7.75	12.63	21.89
2,4,6-Trimethylphenol	2.5474	8.45	16.60	10.87	3.70	0.16	12.05	2.71	2.78	4.42	15.28	12.64
4-Isopropylphenol	2.6361	0.05	45.47	40.31	10.41	0.12	39.08	6.36	3.87	7.67	42.74	40.31
3-n-Propylphenol + 3-ethyl-5-methylphenol	2.7187	11.09	34.17	29.29	55.08	0.92	43.16	10.34	5.98	19.17	30.59	43.91
3-Ethyl-4-methylphenol	2.8716	nq	4.52	3.24	2.04	0.36	5.64	1.26	2.61	1.34	4.36	5.83
2,3,6-Trimethylphenol	2.8720	2.34	10.76	7.70	4.83	0.85	13.52	3.00	6.24	3.17	10.40	13.97
2,3,5-Trimethylphenol	2.9908	0.02	18.09	13.70	17.90	1.39	19.13	5.75	3.11	9.78	14.95	19.00

4-n-Propylphenol	3.0000	3.95	12.21	9.25	12.11	0.94	12.92	1.94	2.11	6.62	10.10	12.83
Sum unknown C3-AP		9.33	41.66	31.61	18.29	1.72	36.50	19.14	6.87	19.10	33.86	36.94
Sum total C3-alkylphenols		45.72	214.70	171.60	149.06	7.89	217.05	56.38	40.59	81.98	188.84	221.36
C4-alkylphenols												
2-tert-Butylphenol	2.4683	0.234	1.684	1.252	1.071	0.077	1.696	0.122	0.504	0.281	1.958	1.950
2,3,5,6-Tetramethylphenol	2.5872	5.417	19.444	17.874	1.341	1.459	13.668	3.373	2.489	6.849	17.838	13.449
3-tert-Butylphenol	2.8624	0.170	0.057	0.059	0.093	0.001	0.134	0.042	0.078	0.046	0.061	0.133
5-Isopropyl-3-methylphenol	3.1440	5.123	9.699	7.146	9.500	0.689	10.955	1.722	1.271	4.459	7.684	11.031
4-tert-Butylphenol	3.3435	0.514	0.653	0.590	0.191	0.164	0.606	0.287	0.565	0.446	0.176	0.621
4-sec-Butylphenol	3.5263	1.378	13.497	10.408	8.985	0.118	14.204	0.605	1.418	0.494	11.296	14.321
4-Isopropyl-3-methylphenol	3.6870	0.685	2.468	1.957	0.384	0.017	1.890	0.348	0.268	0.270	2.027	1.807
4-n-butylphenol	4.0000	0.127	1.032	0.793	1.478	0.022	0.970	0.635	0.153	0.274	0.895	0.975
5-Methyl-4-isopropylphenol	4.0934	0.018	0.159	0.106	0.023	0.014	0.076	0.104	0.034	0.086	0.113	0.171
Sum unknown C4-AP		1.935	12.035	6.039	13.002	1.134	10.136	1.688	1.067	2.443	6.942	10.913
Sum total C4-alkylphenols		15.600	60.728	46.225	36.068	3.696	54.335	8.925	7.849	15.649	48.991	55.371
C5-alkylphenols												
4-tert-Butyl-2-methylphenol	3.3130	0.069	0.354	0.307	0.081	0.029	0.274	0.065	0.049	0.112	0.420	0.286
2-tert-Butyl-4-methylphenol	3.3296	0.981	1.760	1.281	0.037	0.097	1.058	0.285	0.124	0.494	1.390	1.123
2-tert-Butyl-5-methylphenol	3.3573	0.664	1.838	1.524	3.000	0.280	2.971	0.670	0.641	0.480	1.692	3.072
2-tert-Butyl-6-methylphenol	3.4432	1.398	0.664	0.478	0.084	0.003	0.440	0.051	0.082	0.090	0.589	0.458
4-(1,1-Dimethylpropyl)phenol	4.3855	0.013	0.166	0.131	0.216	0.016	0.153	0.098	0.036	0.089	0.146	0.150
4-n-Pentylphenol	5.0000	0.118	12.605	9.584	5.652	0.553	8.769	2.075	1.373	4.434	10.139	9.004
Sum unknown C5-AP		3.698	17.387	13.304	9.070	0.978	13.665	3.244	2.305	5.698	14.377	14.093
Sum total C5-alkylphenols		6.941	17.387	13.304	9.070	0.978	13.665	3.244	2.305	5.698	14.377	14.093
C6-alkylphenols **												
2,6-Diisopropylphenol	3.7119	0.2784	1.1275	0.7171	0.0314	0.0222	0.3864	0.0487	0.0293	0.2043	0.8258	0.4040
2-tert-Butyl-4-ethylphenol	3.8615	0.0184	nd	0.0005	0.0023	nd	0.0242	0.0029	0.0029	nd	0.0319	0.0282
4-(1,1-Dimethylbutyl)phenol	5.1009	0.0223	0.0234	0.0126	0.0285	0.0063	0.0159	0.0110	0.0048	0.0168	0.0178	0.0251
4-(1,2,2-Trimethylpropyl)phenol	5.3609	0.0054	0.0082	0.0028	0.0074	0.0028	0.0237	0.0090	0.0022	0.0078	0.0041	0.0080
4-n-Hexylphenol	6.0000	0.0237	0.0015	nd	0.0091	0.0234	nd	nd	nd	nd	nd	nd
Sum unknown C6-AP		1.1526	2.9516	1.9201	1.0165	0.1972	1.5494	0.4203	0.3507	1.0714	2.3329	1.5468
Sum total C6-alkylphenols		1.5009	4.1123	2.6531	1.0951	0.2519	1.9997	0.4919	0.3898	1.3002	3.2126	2.0121
C7-alkylphenols												
4-(1-Ethyl-1-methylpropyl)-2-methylphenol	5.7248	0.0005	0.0223	0.0113	0.0063	0.0002	0.0089	nd	0.0026	0.0047	0.0212	0.0096
4-(1,1-Dimethylpentyl)phenol	5.9419	0.0019	0.0017	0.0007	0.0004	0.0025	0.0004	0.0027	0.0005	0.0017	0.0010	0.0006
4-n-Heptylphenol	7.0000	0.0093	0.0219	0.0121	0.0349	0.0049	0.0214	0.0640	0.0052	0.0153	0.0243	0.0255

Sum unknown C7-AP	0.1704	0.4544	0.2814	0.1627	0.0434	0.1802	0.0677	0.0579	0.1529	0.3800	0.1526
Sum total C7-alkylphenols	0.1822	0.5003	0.3056	0.2043	0.0510	0.2109	0.1344	0.0662	0.1746	0.4266	0.1883
C8-alkylphenols											
4-tert-Octylphenol	6.3786	0.0050	0.0133	nq	nq	nq	0.0134	nq	0.0029	nq	0.0178
4-n-Octylphenol	8.0000	0.1872	0.0064	0.0040	0.0065	0.0364	0.0043	0.0014	0.0466	0.0109	0.0054
Sum unknown C8-AP		0.1553	0.1122	0.0692	0.0763	0.1003	0.0982	0.0732	0.4564	0.1298	0.1212
Sum total C8-alkylphenols		0.3475	0.1320	0.0732	0.0828	0.1368	0.1025	0.6353	0.0747	0.5059	0.1444
C9-alkylphenols **											
4-n-Nonylphenol	9.0000	0.0001	nq	nd	nd	0.0014	0.0031	0.0038	nq	0.0120	0.0036
Totals											
Total tertiary para-alkylphenols		0.631	1.740	1.401	0.399	0.208	1.370	0.439	0.706	1.229	1.427
Total unknown alkylphenols		16.445	69.823	49.500	38.196	3.747	57.235	23.915	9.793	27.657	58.681
Total alkylphenols		245.0	6003.5	5890.9	34999.7	759.8	19228.6	3856.0	4721.3	1477.4	6785.7
											19873.4

* - without HCl.

** - 2,5-Diisopropylphenol and 2-methyl-4-tert-octylphenol were below limit of quantification in all samples.

Table 5. A selection of unidentified alkylphenols, found in produced water.

Unidentified alkylphenols (arbitrarily assigned number)	APRI	Concentration, µg/l (Average for 9 locations)
C3		
1	2.1560	0.490
2	2.3425	3.510
3	2.4771	0.574
4	2.5168	5.969
5	3.0471	5.678
6	3.0748	1.219
7	3.1939	0.693
8	3.4598	0.939
9	3.6094	1.464
C4		
10	3.2465	6.587
12	3.4571	1.336
C5		
17	3.8615	0.657
19	4.0000	1.087
C6		
22 <i>cl</i>	4.6175	0.118
29 <i>cl</i>	4.8584	0.077
C7		
1 <i>cl</i>	4.4940	0.021
8 <i>cl</i>	4.7590	0.029
C8		
29	7.7682	0.027
35	8.6786	0.028

cl – cluster.

596

597 Fig.1

Figure 2. Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion chromatograms of a standard solution of known alkylphenols (a) as compared to produced water samples (b) for ion masses 330 (C3-alkylphenols), 344 (C4-alkylphenols) and 358 (C5-alkylphenols).

Figure 3. Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion chromatograms of derivatised produced water sample from Statford B oil platform, for two ion masses. Ion 358: C7-alkylphenol derivatives. Ion 356: the unknown compounds.