



HAL
open science

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

Stepan Boitsov, Svein A. Mjøs, Sonnich Meier

► **To cite this version:**

Stepan Boitsov, Svein A. Mjøs, Sonnich Meier. Identification of Estrogen-Like Alkylphenols in Produced Water from Offshore Oil Installations. *Marine Environmental Research*, 2007, 64 (5), pp.651. 10.1016/j.marenvres.2007.07.001 . hal-00562986

HAL Id: hal-00562986

<https://hal.science/hal-00562986>

Submitted on 4 Feb 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

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

Stepan Boitsov, Svein A. Mjøs, Sonnich Meier

PII: S0141-1136(07)00089-X
DOI: [10.1016/j.marenvres.2007.07.001](https://doi.org/10.1016/j.marenvres.2007.07.001)
Reference: MERE 3134

To appear in: *Marine Environmental Research*

Received Date: 27 February 2007
Revised Date: 28 June 2007
Accepted Date: 2 July 2007



Please cite this article as: Boitsov, S., Mjøs, S.A., Meier, S., Identification of Estrogen-Like Alkylphenols in Produced Water from Offshore Oil Installations, *Marine Environmental Research* (2007), doi: [10.1016/j.marenvres.2007.07.001](https://doi.org/10.1016/j.marenvres.2007.07.001)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

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

2 Installations

3 Stepan Boitsov,^{1,*} Svein A. Mjøs² and Sonnich Meier¹

4

5 1. Institute of Marine Research (IMR), Bergen, Norway

6 2. Norwegian Institute of Fisheries and Aquaculture Research (NIFAR), Bergen, Norway

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

* To whom the correspondence is to be addressed. Fax: +47-55238555, email: stepan.boitsov@imr.no

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

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

72 In addition to alkylphenols, thiophenols and naphthols have also been included in
73 the analysis. These compounds have not previously been studied in produced water; however,
74 their presence in oil has been shown (Beens and Tijssen, 1997; Thomson *et al.*, 1997) and
75 their toxicity towards bacteria or higher marine organisms investigated (Londry and Suflita,
76 1998; Falk-Petersen *et al.*, 1985; Cajaraville *et al.*, 1989). These two classes of compounds
77 can undergo pentafluorobenzoyl derivatisation (Thomson *et al.*, 1997) and may therefore be
78 analysed by the same procedure as the one used for alkylphenols.

79

80 **2. Materials and Methods**

81 2.1. Sampling strategy

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

- 93 1. 2 large-volume (100 l) samples from Statfjord A and Statfjord B oil installations
94 (sampled on January 28 and 29, 2005), to be used for qualitative analysis of even
95 minute concentrations of unknown alkylphenols;

- 96 2. 9 regular volume (100 ml) samples from all oil installations except Statfjord B
97 (sampled on various dates in August 2005), to be used for quantitative analysis of
98 known alkylphenols;
- 99 3. 2 regular volume (100 ml) samples from Statfjord C and Oseberg C oil installations,
100 without HCl added (sampled in August 2005, simultaneously with the samples to
101 which HCl was added), to be used for checking the efficiency of the conservation
102 procedure.

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

108

109 (Figure 1)

110

111 2.2. Chemicals and syntheses

112

113 2.2.1. Chemicals

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

126

127 2.2.2. Syntheses

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

130 the desired selectivity. Syntheses of long-chain tertiary alkylphenols have been carried out at
131 the University of Bergen according to the two following procedures. An acid-catalysed
132 reaction between phenol and substituted alcohols leads to pure single isomer products (Huston
133 and Hsieh, 1936); another one with phenol and an isoalkene as substrates and an ion-
134 exchange resin as catalyst yields a mixture of the corresponding *ortho*- or *para*-alkylphenol
135 isomers (Loev and Massengale, 1957). The first procedure was used for specific syntheses of
136 3 *para-tert*-alkylphenols and the second one for non-specific syntheses of mixtures of various
137 tertiary alkylphenol isomers. Products were recrystallised consecutively from pure
138 dichloromethane and a hexane-dichloromethane 3:1 mixture and dried in oil vacuum (in case
139 of solid product), or the solvent was removed by rotor vapour (in case of liquid product).
140 Products were then analysed by GC-MS (full scan) and by 400 MHz ^1H nuclear magnetic
141 resonance (NMR) with deuteriochloroform (CDCl_3) used as NMR solvent and reference. Only
142 pure products were analysed by NMR since NMR spectra of the mixtures could not be
143 resolved. The products of the syntheses are described in Table 1.

144

145

(Table 1)

146

147 2.3. Extraction and purification

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

154

155

156

157

158

159

160

161

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.

162

163

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

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

171

172 2.3.1. GPC

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

183

184 2.3.2. NP-LC

185 After GPC cleanup, the solvent was exchanged to hexane and samples were subjected to NP-
186 LC cleanup and fractionation. For this, the same Gilson fractioning system and Pharmacia
187 fluorescence detector as for GPC was used, but the NP-LC pump was from Shimadzu (LC-9A
188 with FCV-9AL low-pressure solvent mixer). The NP-LC column (150x4.6mm, LiChrosorb
189 60-5 Si) was from Varian (Middelburg, the Netherlands). Injection volume was 500 µl at a
190 time. A gradient of 0 to 6% isopropanol in hexane was used as mobile phase. Fractions of 4
191 ml were collected from 0 to 30 min.

192 15 fractions were obtained, with alkylphenols being concentrated in fraction 8 (from
193 14 to 16 min), up to 97% according to GC-FID measurements. Other polar compounds eluted
194 in fractions 4-15, while PAH and other non-polar hydrocarbons eluted in fractions 1-3. All the
195 NP-LC fractions were then derivatised by pentafluorobenzoyl chloride as described
196 previously (Boitsov *et al.*, 2004). 2 compounds in fraction 8 have been identified as belonging
197 to the naphthol class, one of them being 2-naphthol.

198

199 2.4. GC-MS analysis

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

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

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

213 A Varian Factor Four VF-5ms (Varian, Lake Forest, CA, USA), $L = 50$ m, I.D. =
214 0.25 mm, $df = 0.25$ μ m, was used as analytical column. Helium (99.9%) was used as carrier
215 gas in 22 cm/s constant flow mode. The samples (1 μ l hexane solution) were injected in
216 splitless mode and the split valve was opened after 2 min. The GC program was optimised for
217 alkylphenol analyses as described by Mjøs *et al.* (2006). The oven temperature was 60°C at
218 injection. After 2 min the temperature was increased to 100°C by a temperature programming
219 rate of 30°C/min, which was followed by a second rate of 2°C/min to a final temperature of
220 260°C. Dwell time per ion for all ions was 100 ms. In SIM mode, the total chromatogram was
221 divided into 5 windows (after solvent delay, 10 min), each of these scanned for 4 to 5 selected
222 ions to achieve better sensitivity. The corresponding parameters are shown in Table 2.

223

224

(Table 2)

225

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

230

231 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

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

234

235 3. Results and discussion

236 3.1. Qualitative analysis: large-volume samples.

237

238 3.1.1. Alkylphenols.

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

242

243 (Figure 2)

244

245 (Table 3)

246 Here we have employed a variety of methods in an attempt to characterize the unidentified
247 alkylphenols. Large produced water samples (100 l) from Statfjord A and Statfjord B
248 platforms were used for the detailed, non-quantitative investigations described below. More
249 than 350 compounds have been definitely or tentatively identified as alkylphenols with up to
250 8 carbon atoms in the alkyl substituents, by means of visual investigation of mass spectra. Of
251 these, 305 peaks belonged to unidentified alkylphenols, which is apparent from m/z 195 (EI)
252 belonging to the pentafluorobenzoate fragment, and the corresponding molecular peak for
253 each alkylphenol; the rest were identified by means of the available standard.

254 The alkylphenol retention indices, APRI, developed for this work (Mjøs *et al.*,
255 2006), have been used to systematise all the detected alkylphenols. APRI can be calculated by
256 the following equation (1):

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

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

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

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

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

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

298

299 3.1.2. Thiophenols.

300 No compounds of thiophenol class have been found in the studied samples. The absence of
301 thiophenols could be partly due to the pre-analysis sample preparation procedure that was not
302 optimised for this type of compounds. However, the large volume of the analysed samples,
303 1000 times larger than the regular volume used for routine analysis of produced water at our
304 laboratory, allows to suggest that the amounts of thiophenols in produced water are
305 insignificant.

306

307 3.1.3. Naphthols.

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

313

314 3.1.4. Other compounds.

315 A large number of unidentified compounds with molecular masses 328, 342, 356, 370 and
316 384 have been determined in the produced water samples. The same type of compounds have
317 previously been observed in produced water from the Oseberg C oil installation (Boitsov *et*.
318 *al.*, unpublished results). The masses differ by 2 from C₃-C₇ alkylphenol
319 pentafluorobenzoates; however, the relative amounts of the compounds are comparable to or
320 even larger than those of the corresponding alkylphenols (Fig. 3). Similar compounds with
321 masses differing by 4 from masses of alkylphenol derivates have also been observed.

322

323

(Figure 3)

324

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

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

333

334 3.2. Quantitative analysis: regular volume samples.

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

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

352

353 (Table 4)

354

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

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

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

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

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

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

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

406

407 (Table 5)

408

409 **4. Conclusion**

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

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

428

429 **5. Acknowledgements**

430 We are grateful to Research Council of Norway for financial support, to Professor Jon
431 Songstad for valuable discussion and for laboratory facilities, to Dr. Nils Åge Frøystein for
432 the help with interpretation of NMR spectra, to Dr. Craig Morton for the help with the English
433 and to Julie Andersen for the help with creating the map.

ACCEPTED MANUSCRIPT

434 **6. References**

435

436

Beens, J., and Tijssen, R. (1997). The characterization and quantitation of sulfur-

437

containing compounds in (heavy) middle distillates by LC-GC-FID-SCD. *Journal of High*

438

Resolution Chromatography, 20, 131-137.

439

440

Boitsov, S., Meier, S., Klungsøyr, J., and Svardal, A. (2004). Gas chromatography–mass

441

spectrometry analysis of alkylphenols in produced water from offshore oil installations as

442

pentafluorobenzoate derivatives. *Journal of Chromatography A*, 1059, 131-141.

443

444

Brodskii, E.S., Lukashenko, I.M., Lebedevskaya, V.G., and Polyakova, A.A. (1973).

445

Determination of isomer and homolog composition of alkylphenols by molecular mass

446

spectrometry. *Chemistry and Technology of Fuels and Oils*, 9, 645-650.

447

448

Børseth, J.F., and Tollefsen, K.-E. (2004). Water column monitoring 2003 – summary

449

report. Rogalandforskning report nr. 2004/039, RF, Stavanger, Norway, pp. 28.

450

451

Cajaraville, M.P., Marigomez, J.A., and Angulo, F. (1989). Stability of 1-naphthol in sea-

452

water solutions and its uptake by the marine prosobranch gastropod *Littorina-Littorea (L)*.

453

Bulletin of Environmental Contamination and Toxicology, 42, 799-806.

454

455

Dallüge, J., Beens, J., and Brinkman, U.A.T. (2003). Comprehensive two-dimensional gas

456

chromatography: a powerful and versatile analytical tool. *Journal of Chromatography A*,

457

1000, 69-108.

458

- 459 De Juan, A., and Tauler, R. (2003). Chemometrics applied to unravel multicomponent
460 processes and mixtures - Revisiting latest trends in multivariate resolution. *Analytica*
461 *Chimica Acta*, 500, 195-210.
- 462
- 463 Falk-Petersen, I.-B., Kjørsvik, E., Lønning, S., Naley, A.M., and Sydnes, L.K. Toxic
464 effects of hydroxilated aromatic hydrocarbons on marine embryos. (1985). *Sarsia*, 70, 11-
465 16.
- 466
- 467 Grøsvik, B.-E., Meier, S., Westheim, K., Skarphéðinsdóttir, H., Liewenborg, B., Balk, L.,
468 and Klungsøyr, J. (2007). Condition monitoring in the water column 2005: Oil
469 hydrocarbons in fish from Norwegian waters. Institute of Marine Research report nr. 2-
470 2007, IMR, Bergen, Norway, pp. 33.
- 471
- 472 Huston, R.C., and Hsieh, T.Y. (1936). Condensation of aliphatic alcohols with aromatic
473 compounds in the presence of aluminium chloride. *Journal of the American Chemical*
474 *Society*, 58, 439-441.
- 475
- 476 Kohtani, S., Hiro, J., Yamamoto, N., Kudo, A., Tokumura, K., and Nakagaki, R. (2005).
477 Adsorptive and photocatalytic properties of Ag-loaded BiVO₄ on the degradation of 4-n-
478 alkylphenols under visible light irradiation. *Catalysis Communications*, 6, 185-189.
- 479
- 480 Liang, Y.-Z., Kvalheim, O., and Manne, R. (1993). White, gray and black
481 multicomponent systems – a classification of mixture problems and methods for their
482 quantitative analysis. *Chemometrics and Intelligent Laboratory Systems*, 18, 235-250.
- 483

- 484 Loev, B., and Massengale, J.T. (1957). Cation exchange resins as catalysts in the
485 alkylation of phenols. *Journal of Organic Chemistry*, 22, 988-989.
- 486
- 487 Londry, K.L., and Suflita, J.M. (1998). Toxicity effects of organosulfur compounds on
488 anaerobic microbial metabolism. *Environmental Toxicology and Chemistry*, 17, 1199-
489 1206.
- 490
- 491 Meier, S., Klungsøyr, J., Boitsov, S., Eide, T., and Svardal, A. (2005). Gas
492 chromatography–mass spectrometry analysis of alkylphenols in cod (*Gadus morhua*)
493 tissues as pentafluorobenzoate derivatives. *Journal of Chromatography A*, 1062, 255-268.
- 494
- 495 Meier, S., Andersen, T.E., Norberg, B., Thorsen, A., Taranger, G.L., Kjesbu, O.S., Dahle,
496 R., Morton, H.C., Klungsøyr, J., and Svardal, A. (2007). Effects of alkylphenols on the
497 reproductive system of Atlantic cod (*Gadus morhua L.*) *Aquatic Toxicology*, 81, 207-218.
- 498
- 499 Mjøs, S.A. (2003). Spectral transformations for deconvolution methods applied on gas
500 chromatography-mass spectrometry data. *Analytica Chimica Acta*, 488, 231-241.
- 501
- 502 Mjøs, S.A., Meier, S., and Boitsov, S. (2006). Alkylphenol retention indices. *Journal of*
503 *Chromatography A*, 1123, 98-105.
- 504
- 505 Moeder, M., Martin, C., Schlosser, D., Harynuk, J., Górecki, T. (2006). Separation of
506 technical 4-nonylphenols and their biodegradation products by comprehensive two-
507 dimensional gas chromatography coupled to time-of-flight mass spectrometry. *Journal of*
508 *Chromatography A*, 1107, 233-239.

509

510 Myhre, L.P., Bausant, T., Sundt, R., Sanni, S., Vabø, R., Skjoldal, H.R., Klungsøyr, J.
511 (2004). Risk assessment of reproductive effects of alkylphenols in produced water on fish
512 stocks in the North Sea. Akvamiljø report AM-2004/018, RF-Akvamiljø, Stavanger,
513 Norway, pp. 76.

514

515 Nimrod, A.C., and Benson, W.H. (1996). Environmental estrogenic effects of alkylphenol
516 ethoxylates. *Critical Reviews in Toxicology*, 26, 335-364.

517

518 NPD. (2006). Norwegian Petroleum Directorate (NPD) press release 20/2006, 16.06.2006.

519 Available online at

520 http://www.npd.no/Norsk/Aktuelt/Pressemeldinger/2006/pressemelding_20_2006.htm (*in*

521 *Norwegian*).

522

523 OLF. (2003). Recommended guidelines for the sampling and analysis of produced water.

524 The Norwegian Oil Industry Association (OLF) Guidelines No. 85, pp 14.

525

526 OLF. (2006). Environmental report 2005. The Norwegian Oil Industry Association (OLF),

527 Stavanger, Norway, pp. 58. For the online version, as well as for field-specific data on

528 discharges, see <http://www.olf.no/miljo/miljorapporter/?32711> .

529

530 Orjala, J., Mian, P., Rali, T., and Sticher, O. (1998). Gibbilimbols A-D, cytotoxic and

531 antibacterial alkenylphenols from Piper gibbilimum. *Journal of Natural Products*, 61,

532 939-941.

533

- 534 Routledge, E.J., and Sumpter, J.P. (1997). Structural features of alkylphenolic chemicals
535 associated with estrogenic activity. *Journal of Biological Chemistry*, 272, 3280-3288.
536
- 537 Ruß, A.S., Vinken, R., Schuphan, I., and Schmidt, B. (2005). Synthesis of branched *para*-
538 nonylphenol isomers: occurrence and quantification in two commercial mixtures.
539 *Chemosphere*, 60, 1624-1635.
540
- 541 Scott, A.P., Kristiansen, S.I., Katsiadaki, I., Thain, J., Tollefsen, K.-E., Goksøyr, A., and
542 Barry, J. (2006). Assessment of oestrogen exposure in cod (*Gadus morhua*) and saithe
543 (*Pollachius virens*) in relation to their proximity to an oilfield. In: Biological effects of
544 contaminants in marine pelagic ecosystems. Eds. Hylland, K., Lang, T., and Vethaak, D.
545 Special publication of Society of Environmental Toxicology and Chemistry (SETAC), pp.
546 329-339.
547
- 548 Snyder, S.A., Keith, T. L., Naylor, C.G., Staples, C.A., and Giesy, J.P. (2001).
549 Identification and quantitation method for nonylphenol and lower oligomer nonylphenol
550 ethoxylates in fish tissues. *Environmental Toxicology and Chemistry*, 20, 1870-1873.
551
- 552 Thomas, K.V., Balaam, J., Hurst, M.R., and Thain, J.E. (2004a). Bio-analytical and
553 chemical characterisation of offshore produced water effluents for estrogen receptor (ER)
554 agonists. *Journal of Environmental Monitoring*, 6, 593-598.
555
- 556 Thomas, K.V., Balaam, J., Hurst, M.R., and Thain, J.E. (2004b). Identification of *in vitro*
557 estrogen and androgen receptor agonists in North Sea offshore produced water discharges.
558 *Journal of Environmental Toxicology and Chemistry*, 23, 1156-1163.

559

560 Thomson, J.S., Green, J.B., and McWilliams, T.B. (1997). Determination of sulfides and
561 thiols in petroleum distillates using solid-phase extraction and derivatization with
562 pentafluorobenzoyl chloride. *Energy & Fuels*, 11, 909-914.

563

564 Tollefsen, K.-E., Harman, C., Smith, A. and Thomas, K.V. (2007). Estrogen receptor (ER)
565 agonists and androgen receptor (AR) antagonists in effluents from Norwegian North Sea
566 oil production platforms. *Marine Pollution Bulletin* 54, 277-283.

ACCEPTED MANUSCRIPT

567 **Figure captions**

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

569

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

574

575 **Figure 3.** Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion
576 chromatograms of derivatised produced water sample from Statfjord B oil platform, for two
577 ion masses. Ion 358: C7-alkylphenol derivates. 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 (<i>t</i>), 1.04-1.15 (<i>m</i>), 1.27 (<i>s</i>), 1.52-1.58 (<i>m</i>), 3.98 (<i>s</i>), 6.76-6.81 (<i>d</i>), 7.18-7.24 (<i>d</i>).
Pure C ₆ -alkylphenol	<i>4-(1-methyl-2,2-dimethylpropyl)phenol</i> .	Yellow crystals.	0.73-0.78 (<i>d</i>), 1.22 (<i>s</i>), 1.81-1.89 (<i>m</i>), 3.99 (<i>s</i>), 6.73-6.80 (<i>d</i>), 7.16-7.23 (<i>d</i>).
Pure C ₇ -alkylphenol	<i>4-(1,1-dimethylpentyl)phenol</i> .	Black oily liquid.	0.80-0.87 (<i>t</i>), 0.99-1.08 (<i>m</i>), 1.17-1.25 (<i>m</i> , unres.) 1.27 (<i>s</i>), 1.52-1.60 (<i>m</i>), 3.98 (<i>s</i>), 6.74-6.80 (<i>d</i>), 7.17-7.23 (<i>d</i>).
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.	-

579

580 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

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

582

583

584 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

585

586

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

Compound	APRI	Oil installations										
		Troll B	Statfjord A	Statfjord C	Åsgard B	Grane	Oseberg C	Heidrun	Snorre A	Gullfaks B	Statfjord C*	Oseberg 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												
<i>o</i> -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
<i>m</i> -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
<i>p</i> -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- <i>n</i> -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- <i>n</i> -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	<i>nq</i>	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- <i>tert</i> -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- <i>tert</i> -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- <i>tert</i> -Butylphenol	3.3435	0.574	0.653	0.590	0.791	0.164	0.606	0.287	0.565	0.446	0.176	0.621
4- <i>sec</i> -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- <i>tert</i> -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- <i>tert</i> -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- <i>tert</i> -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- <i>tert</i> -Butyl-6-methylphenol	3.4432	1.398	1.838	0.664	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	0.166	0.166	0.131	0.016	0.553	8.769	2.075	1.373	4.434	10.139
Sum unknown C5-AP		3.698	12.605	9.584	5.652	0.553	8.769	2.075	1.373	4.434	10.139	9.004
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- <i>tert</i> -Butyl-4-ethylphenol	3.8615	0.0184	<i>nd</i>	0.0005	0.0023	<i>nd</i>	0.0242	0.0029	0.0029	<i>nd</i>	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	<i>nd</i>	0.0091	0.0234	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
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	<i>nd</i>	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	0.0938	0.0014	0.0466	0.0109	0.0054
Sum unknown C8-AP	0.1553	0.1122	0.0692	0.0763	0.1003	0.0982	0.5282	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	0.1407	0.1444
C9-alkylphenols **											
4-n-Nonylphenol	9.0000	0.0001	nq	nd	0.0014	0.0031	0.0038	nq	0.0120	0.0036	nd
Totals											
Total tertiary para-alkylphenols	0.631	1.740	1.401	0.399	0.208	1.370	0.439	0.706	0.681	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	53.782	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.

590

591

592

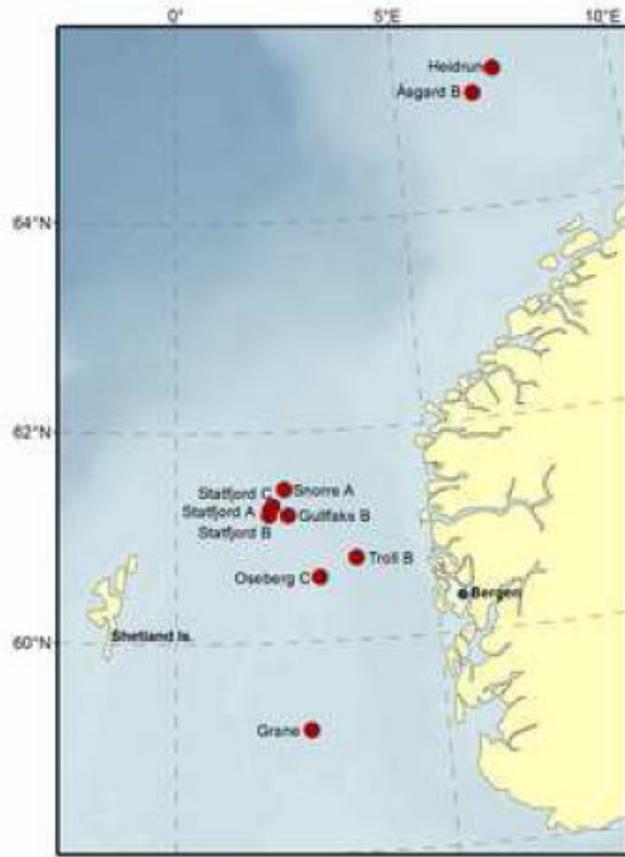
593 Table 5. A selection of unidentified alkylphenols, found in produced water.

Unidentified alkylphenols (arbitrarily assigned number)	APRI	Concentration, $\mu\text{g/l}$ (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.

594

595



596

597 Fig.1

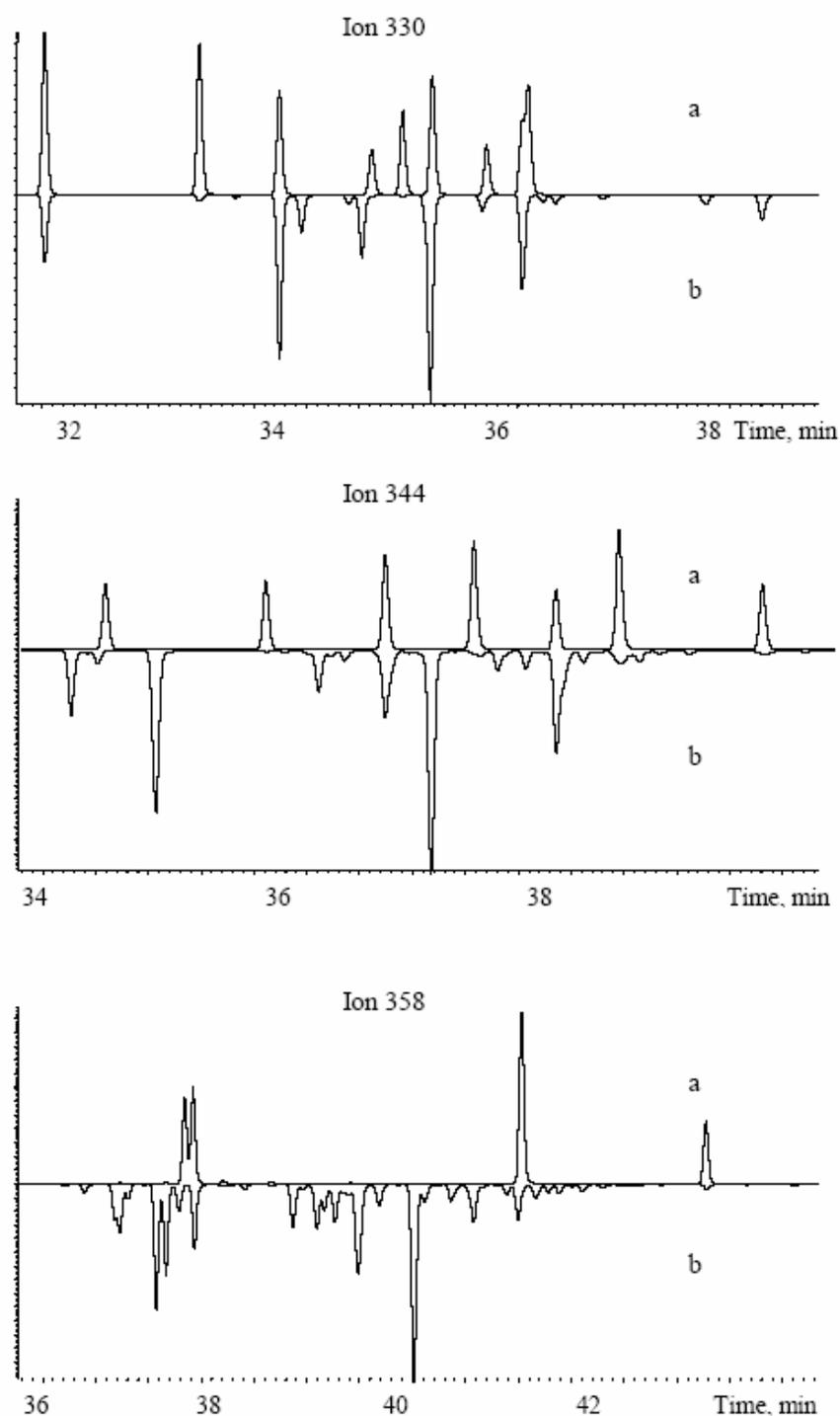


Figure 2. Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion chromatograms of a standard solution of known alkylphenols (a) as compared to produced water samples (b) for ion masses 330 (C3-alkylphenols), 344 (C4-alkylphenols) and 358 (C5-alkylphenols).

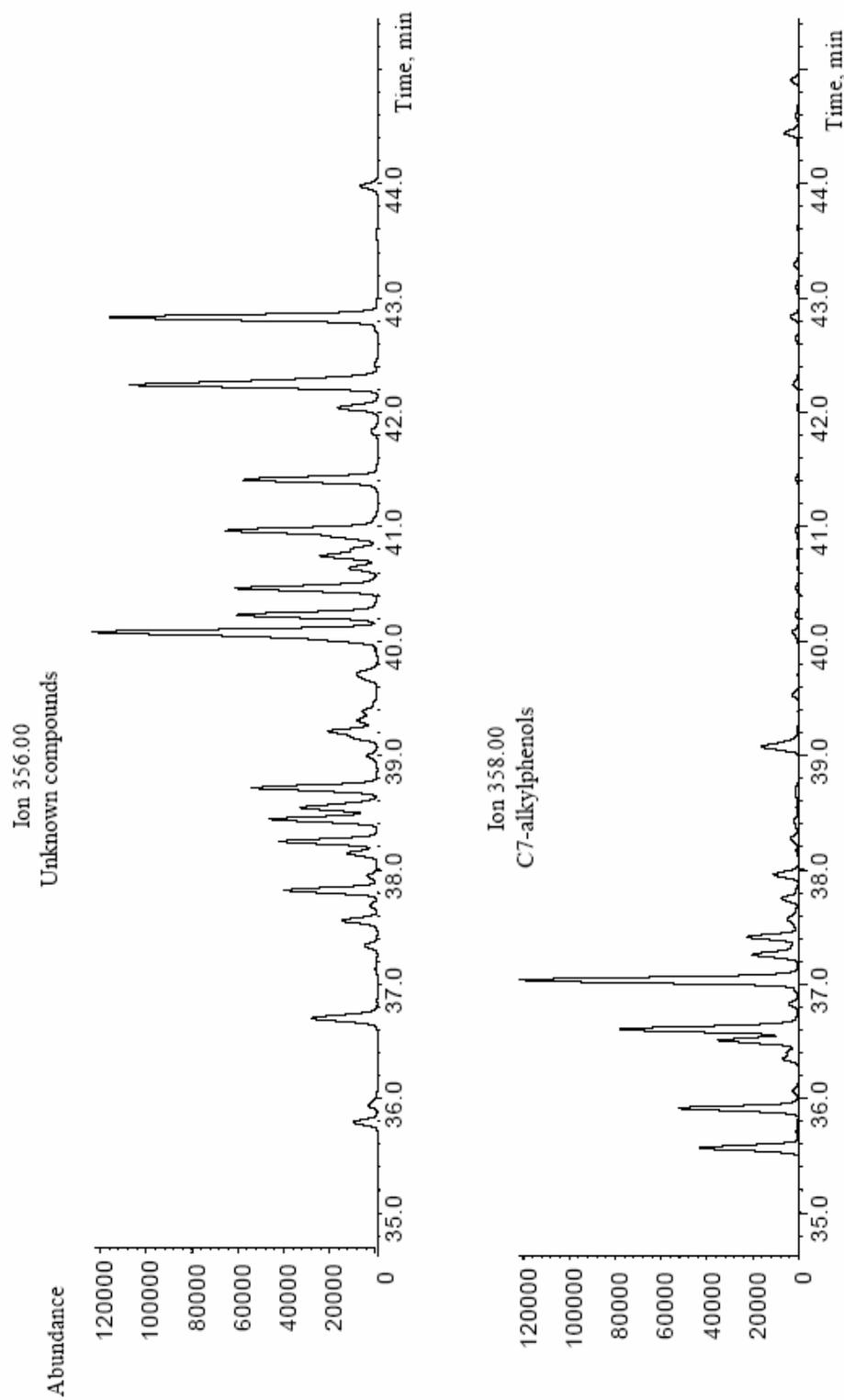


Figure 3. Negative chemical ionisation (NCI), selected ion monitoring (SIM) ion chromatograms of derivatised produced water sample from Statford B oil platform, for two ion masses. Ion 358: C7-alkylphenol derivatives. Ion 356: the unknown compounds.