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The effect of oxidation on the distribution of alkylphenols in crude oils

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Abstract

Alkylphenols in crude oils can be affected by oxidation during storage. A crude oil and an alkylphenol mixture were exposed to light and air for various time periods, resulting in significant alterations of the alkylphenol distributions. Most affected were *ortho/para* substituted isomers, such as 2,4-/2,6-dimethylphenol and 2,4,6-trimethylphenol, whereas phenol, and *meta* substituted isomers such as *m*-cresol and 3,5-dimethylphenol were least affected. The alkylphenol distributions in two crude oils from the same accumulation, one of which was stored for 34 years, were found to be different in a manner consistent with a scenario where the stored oil had been affected by oxidation. These results suggest that the alkylphenol distributions in crude oils can be severely altered by oxidation which is enhanced by exposure to light. Therefore, if precautions are not taken to minimise the effects of oxidation during sampling and storage, alkylphenol distributions may be altered. Significant oxidation can be avoided by storing samples in opaque containers such as metal tins and drums and reducing or flushing air from the container's headspace.

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1. Introduction

Alkylphenol distributions have been reported in both crude oils (Ioppolo et al., 1992; Taylor et al., 1997) and oilfield waters (Macleod et al., 1993; Dale et al., 1995). Because of the polar character of these alkylphenols, several authors suggested that their concentration and distribution can be altered by the interaction of petroleum with mineral/organic matrices and subsurface waters in the carrier beds, through partitioning processes during migration and accumulation (Larter and Aplin, 1995; Taylor et al., 1997, 2001). Accordingly, based on studies of the partitioning behaviour of these compounds in laboratory experiments (Taylor, 1994; Ioppolo-Armanios et al., 1995; Bennett and Larter,

1997), alkylphenols have been applied to describe the effects of migration on the composition of crude oils (Bennett et al., 1996; Galimberti et al., 2000; Lucach et al., 2002). Similarly, partitioning processes resulting in the mobilisation of water-soluble compounds have been suggested to change the alkylphenol concentration and distribution in reservoir crude oils (Bennett and Larter, 1997). Recently, the effects of biodegradation on alkylphenols in crude oils have been assessed (Taylor et al., 2001).

Alkylphenols are especially reactive towards oxygen. For instance, it is well known that phenols are oxidised readily and for that reason they are applied as antioxidants (Scott, 1993). For example, one of the most commonly used antioxidants is the phenol BHT (butylated hydroxytoluene), which is used as an anti-oxidant in lipid analyses (Scott, 1993) and as a food preservative (E321). Oxidation of phenols is enhanced by light and photo-oxidation of phenols has been the focus of many

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Table 1
Sample details

Sample	Country	Basin	Probable age	Storage conditions	Type/colour
Barrow	Australia	Carnarvon	Jurassic	Can	Crude oil/Brown
Goodwyn	Australia	Carnarvon	Jurassic	Clear glass	Condensate/Yellow
Legendre (stored)	Australia	Carnarvon	Jurassic	Clear glass	Crude oil/Brown
Legendre (fresh)	Australia	Carnarvon	Jurassic	Drum	Crude oil/Brown

environmental studies (e.g. Canonica and Hoigné, 1995; Gerdes et al., 1997; Sýkora et al., 1997; De et al., 1999). Photo-oxidation results from the excitation of oxygen, which can react readily with compounds containing labile C–H bonds, such as alkylphenols (Scott, 1993). The extent of oxidation decreases with increasing concentration of phenols, due to oxygen being a limiting factor (De et al., 1999; Terzian and Serpone, 1999). These reactions are enhanced by photosensitisers, compounds that absorb light and then excite oxygen, which can range from metal oxides to fulvic acid and humic acids (Gerdes et al., 1997). Terzian and Serpone (1999) have shown that isomeric dimethylphenols are photo-oxidised at different rates in the presence of a photosensitiser, with 2,4- and 2,6-dimethylphenol reacting the fastest and 3,5-dimethylphenol the slowest. More complex naturally occurring photosensitisers such as dissolved natural organic matter (DNOM) have been suggested to play a part in the degradation of phenols in natural water systems (Caponica and Hoigné, 1995).

Although it can be envisaged that crude oil can undergo oxidation during storage, little systematic study of how this process affects the composition of crude oil has been undertaken in geochemistry. For example, it has been suggested that fluorenones (Bennett and Larter, 2000) and sulphoxides (Schouten et al., 1995) in crude oils and rock extracts are formed through oxidation during storage. Another study investigated the abiotic oxidation of petroleum bitumens under natural conditions (Charrié-Duhaut et al., 2000).

Crude oil samples are sometimes stored in glass containers over many years and can therefore become exposed considerably to light. This prompted us to check for evidence of oxidation of alkylphenols in geochemical samples and to assess whether this is a factor to be considered in the handling and storage of crude oils. In this study we report the effect of oxidation on the distribution of alkylphenols in crude oils.

2. Experimental

2.1. Samples

Table 1 lists the samples used in this study, their location and probable source rock age. The stored

sample of Legendre was from an initial drill stem test in 1968 for the discovery well. The fresh sample of Legendre was collected in 2001 when the oilfield was developed.

2.2. Materials

2.2.1. Alkylphenols

Phenol standards were obtained from commercial sources: Aldrich Chemical Company, Sigma Chemicals and Fluka Chemie (Switzerland). These standards were AR grade with purities in excess of 97%.

Alkylphenol identifications that were not available were based on previous identifications by Ioppolo et al. (1992) and Bastow et al. (2003).

2.2.2. Alkylphenol mixture

The alkylphenol mixture for degradation experiments consisted of the following compounds ranging in concentrations from 15 to 40 mg/l (Table 2) in hexane: phenol, 2-bromophenol, *o*-cresol, *p*-cresol, *m*-cresol, 2,6-, 2,4-, 2,5-, 3,5-, 2,3-dimethylphenol, 2,4,6-, 2,3,5-, 3,4,5-trimethylphenol.

Table 2

Alkylphenols remaining from the photo-oxidations of alkylphenol standards for the various time periods

Compound	Alkylphenol conc. mg/l			% Remaining	
	0 h	1 h	2 h	1 h	2 h
Phenol	40	40	39	99	99
<i>o</i> -Cresol	26	25	16	97	63
<i>p</i> -Cresol	31	31	21	101	69
<i>m</i> -Cresol	26	26	27	99	103
2,6-Dimethylphenol	14	1	0	10	1
2,4-Dimethylphenol	32	12	1	38	3
2,5-Dimethylphenol	29	25	7	86	22
4-Ethylphenol	23	23	17	101	74
3,5-Dimethylphenol	39	39	36	102	93
2,3-Dimethylphenol	28	24	7	85	23
2,4,6-Trimethylphenol	24	1	0	2	1
2,3,5-Trimethylphenol	25	16	1	64	3
3,4,5-Trimethylphenol	29	25	7	85	24

2.3. Separation and analysis

The alkylphenol fraction (PHE) separated using the reagents and procedure described by Bastow et al. (2003) is briefly described.

A silica gel column was prepared by taking a glass column (10 cm × 5.7 mm i.d., a Pasteur pipette is used) plugged with a small amount of cotton wool. It was packed dry with activated silica gel (approx. 0.6 g, 55 mm) and was made uniform by passing 3 bed volumes of *n*-pentane under slight pressure (using a pipette teat). The sample (80–100 mg) containing the surrogate standards (*d*₅-phenol, *d*₃-2,6-dimethylphenol and *d*₈-carbazole) in a minimum volume of *n*-pentane (ca. 50 µl), was introduced to the top of the column to produce a concentrated band; additional volumes of pentane (2 × 100 µl) may be used to transfer the sample onto the column.

Saturate and aromatic hydrocarbons (SAA fraction) were eluted from the silica gel column under gravity with *n*-pentane/dichloromethane (9:1 v/v, 4 mL). The phenol/carbazole fraction (PHE fraction) was collected after elution of the saturate and aromatic fraction from the silica gel column, by eluting under gravity with *n*-pentane/ether (7:3 v/v, 5 ml). To provide a sample ready for GC–MS analysis it is necessary to reduce the amount of ether/pentane without loss of volatiles. This was achieved by adding *n*-hexane (2 ml) to the PHE fraction and carefully reducing the solvent by distillation to approx. 2 ml in a vial (22 ml; 75 mm × 19 mm) using a sand bath set at 60 °C, after which the internal standard was added (2-bromophenol). The fraction obtained in this manner contains alkylphenols and alkylcarbazoles.

2.4. Analysis by gas chromatography–mass spectrometry (GC–MS)

A Hewlett-Packard 5973 MSD, interfaced with a HP6890 gas chromatograph was fitted with fused-silica open tubular columns coated with a ZB-5 stationary phase (Phenomenex, 60 m × 0.25 mm i.d., 0.25 µm film thickness). The GC oven temperature was programmed from 40 °C (1 min) to 310 °C (20 min) at 3 °C min⁻¹. Samples for analysis were dissolved in hexane and injected using the vapourising injector with a HP 6890 auto-sampler. Helium was used as carrier gas at a constant flow of 1.0 ml min⁻¹ and the vapourising injector was operated in pulsed splitless mode (30 psi for 0.5 min). Typical MSD conditions were: ionisation energy 70 eV; source temperature 230 °C; electron multiplier voltage 1800 V.

2.5. Laboratory photo-oxidation

2.5.1. Samples (crude oil and alkylphenol mixture)

Samples (1 ml) were placed into glass vials (2 ml) and left in direct sunlight for various time periods, during February in Perth, Australia.

3. Results and discussion

3.1. Samples from the same accumulation

The alkylphenol distributions from the Legendre crude oil that has been stored for 34 years and those of a fresh sample from the same accumulation are markedly different (Fig. 1). The stored crude oil is much less abundant in *o*-cresol, 2,4- and 2,6-dimethylphenol and 2,3,6- and 2,4,6-trimethylphenol than the fresh crude oil. In contrast, phenol, *m*-cresol, 3,5-dimethylphenol and 3-ethyl-5-methylphenol appear to be present in similar relative abundances in both oils. In fact, the absolute concentrations of these compounds are remarkably similar in both samples. For example, the concentration of 3,5-dimethylphenol in the stored sample was measured as 0.55 µg/g and in the fresh sample this was 0.52 µg/g. Conventional saturate and aromatic geochemical parameters measured for these two samples were identical, making them indistinguishable indicating that any differences in alkylphenol distributions between the samples are likely to be attributable to the effects of storage. These results indicate that the alkylphenols in the stored crude oil have undergone significant changes upon storage, which has led to the depletion of alkylphenols such as *o*-cresol, 2,6-/2,4-dimethylphenols and 2,4,6-trimethylphenol (and other trimethylphenols), whereas other alkylphenols like phenol, *m*-cresol, 3,5-dimethylphenol and 3-ethyl-5-methylphenol have remained largely unaltered. This is consistent with photo-oxidation rates of alkylphenols as published by Terzian and Serpone (1999) who showed that *ortho*-substituted isomers of alkylphenols are oxidised at much higher rates than *meta*-substituted isomers. Therefore, we suggest that the stored sample has been affected by oxidation during storage.

3.2. Laboratory photo-oxidations of alkylphenols

To investigate the role that light may play in altering the distributions of alkylphenols, a mixture of alkylphenols (in hexane) was placed into a glass vial and subjected to direct sunlight for various periods. The alkylphenol composition of the original mixture and after 1 and 2 h of sunlight exposure respectively are shown in Fig. 2. The results show that even after 1 h of exposure to sunlight the alkylphenol distribution has been significantly altered. The most striking effect was the almost complete removal of 2,6-dimethylphenol and 2,4,6-trimethylphenol, as well as the substantial reduction of 2,4-dimethylphenol. Further exposure to sunlight (2 h) resulted in more severe changes in alkylphenol distribution producing a distribution dominated by phenol, *m*-cresol and 3,5-dimethylphenol. These experiments show that alkylphenol distributions can be readily altered on exposure to light, resulting in

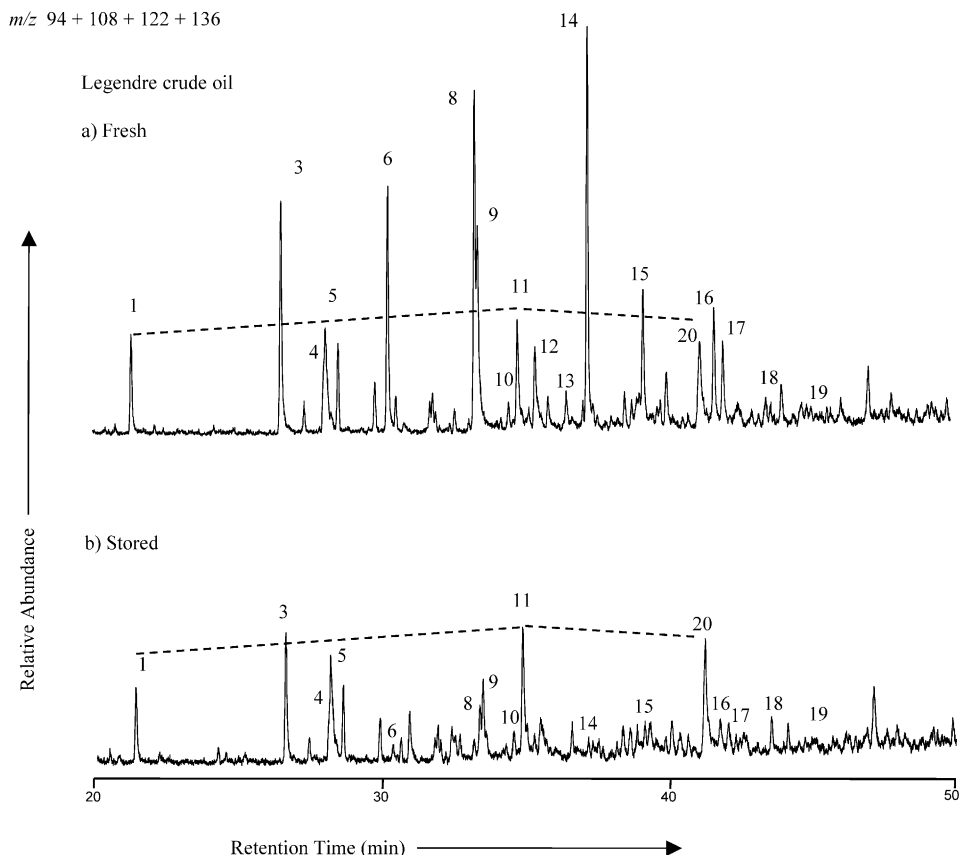


Fig. 1. Partial combined m/z 94 + 108 + 122 + 136 mass chromatograms showing the C_0 , C_1 , C_2 and C_3 alkylphenol distribution in the Legendre crude oil for (a) fresh, and (b) stored. For peak identifications refer to Table 4.

substantial degradation of *ortho*- and *para*- substituted isomers, such as 2,4- and 2,6-dimethylphenol and 2,4,6-trimethylphenol while phenol and *meta*-substituted isomers such as *m*-cresol, 2,5- and 3,5-dimethylphenol remain practically unaffected. The results are summarised in Table 2. Furthermore, the oxidation trends observed for the dimethylphenols are in good agreement with those reported by Terzian and Serpone (1999) who showed that isomeric dimethylphenols are photo-oxidised at different rates in the presence of a photosensitiser, with 2,6- and 2,4-dimethylphenol reacting the fastest and 3,5-dimethylphenol the slowest.

3.3. Laboratory photo-oxidation of a crude oil

In order to assess the effect of photo-oxidation on the alkylphenols in a crude oil and possible effects from constituents in the crude oil, a sample of Barrow crude oil was subjected to direct sunlight in the same manner as the mixture of alkylphenols. Fig. 3 shows the alkylphenol distributions of the original Barrow crude oil and after 20 h of exposure to sunlight. The two distributions are markedly different. Barrow crude oil is

dominated by 2,6/2,4-dimethylphenols and 2,4,6-trimethylphenol, whereas, after 20 h exposure to sunlight the relative abundances of these compounds have substantially decreased. Comparison of these results with the photo-oxidised alkylphenol mixture shows similar effects in both samples. *Ortho*- and *para*-substituted isomers, such as 2,4- and 2,6-dimethylphenol and 2,4,6-trimethylphenol are the most affected. Phenol, *m*-cresol, 3,5-dimethylphenol and 3-ethyl-5-methylphenol are the alkylphenols least affected in both sets of samples. 2,5-Dimethylphenol seems to be more resistant than 2,4-dimethylphenol especially when photo-oxidation has been less severe as observed in the photo-oxidation of the alkylphenol standards. These results are summarised in Table 3, which shows that there has been little change in the *m*-cresol, 3,5-dimethylphenol and 3-ethyl-5-methylphenol concentrations. In addition, the alkylphenol distribution from the photo-oxidised crude oil shows striking similarities to some stored crude oils such as Goodwyn 4 (Fig. 3), suggesting that these crude oils have indeed been affected by oxidation, which can therefore be a problem on storage. It is interesting to note that it takes much longer for the alkylphenols in

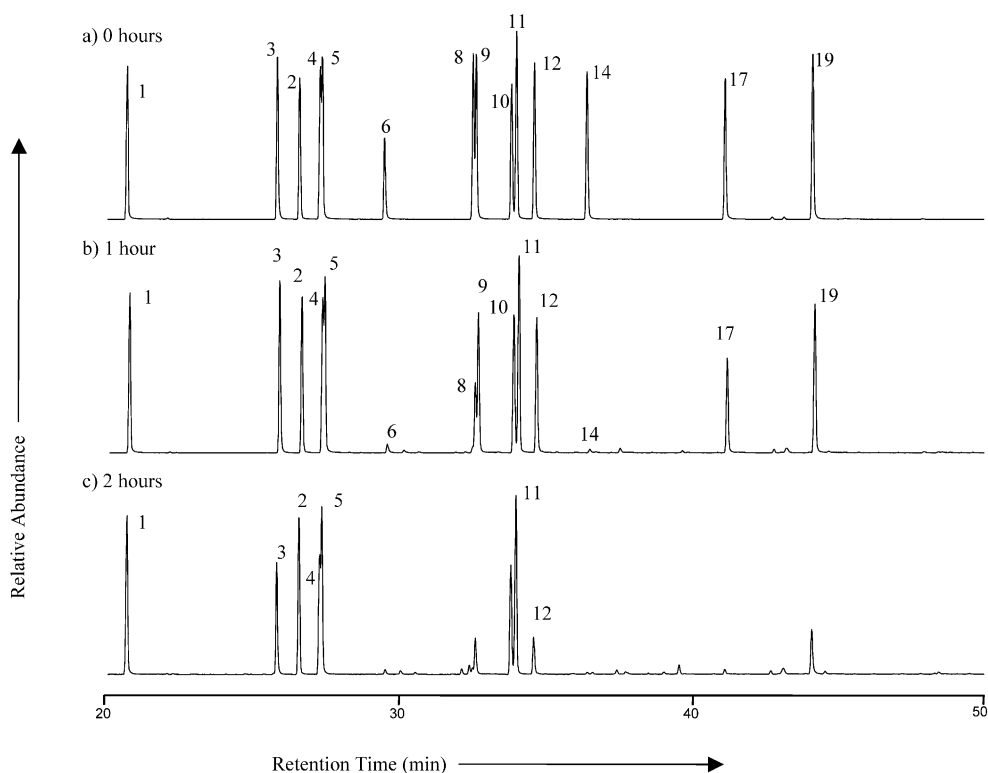


Fig. 2. Partial total ion chromatograms showing the alkylphenol mixture (a) before sunlight, (b) 1 h sunlight, and (c) 2 h sunlight. For peak identifications refer to Table 4.

Barrow crude oil sample to degrade to the same level as in the alkylphenol mixture. This is likely to be a result of the presence of more labile compounds in this crude oil sample which are oxidised in preference to the alkylphenols.

3.4. Oxidation trends in stored samples

The results obtained in this study indicate the possibility that oxidation of alkylphenols occurs during storage. Because it was found that alkylphenols such as phenol, *m*-cresol, 3,5-dimethylphenol and 3-ethyl-5-methylphenol are more resistant to oxidation than other isomers, parameters can be formulated based on the relative abundances of these most resistant phenols. These can then be applied to indicate the extent of oxidation. Two parameters were devised, i.e. 3,5-dimethylphenol/(total C2-phenols) and 3-ethyl-5-methylphenol/(total C3-phenols). If oxidation has affected an oil, both parameters should increase. The parameters were measured for a suite of over a hundred crude oil samples (Fig. 4). A good linear relationship ($r^2=0.77$) was obtained suggesting that many of these crude oils have been affected by oxidation to some extent. The samples previously discussed (Barrow and Legendre crude oils) are also plotted on this figure and show that laboratory

Table 3
Alkylphenols remaining from the photo-oxidation of Barrow crude oil after 20 h of sunlight

Compound	Alkylphenol conc. ng/g		% Remaining
	Original sample	After photo-oxidised	
Phenol	843	725	86
<i>o</i> -Cresol	3563	2619	74
<i>p</i> -Cresol	1326	597	45
<i>m</i> -Cresol	662	734	111
2,6-Dimethylphenol	6880	163	2
2-Ethylphenol	755	541	72
2,4-Dimethylphenol	11914	1387	12
2,5-Dimethylphenol	3768	1505	40
4-Ethylphenol	345	188	55
3,5-Dimethylphenol	896	987	110
2,3-Dimethylphenol	843	399	47
3,4-Dimethylphenol	690	451	66
2,4,6-Trimethylphenol	40910	1240	3
2,3,6-Trimethylphenol	4678	358	8
2,4,5-Trimethylphenol	6240	980	16
2,3,5-Trimethylphenol	2093	612	29
3,4,5-Trimethylphenol	448	132	30
3-Ethyl-5-methylphenol	76	98	129

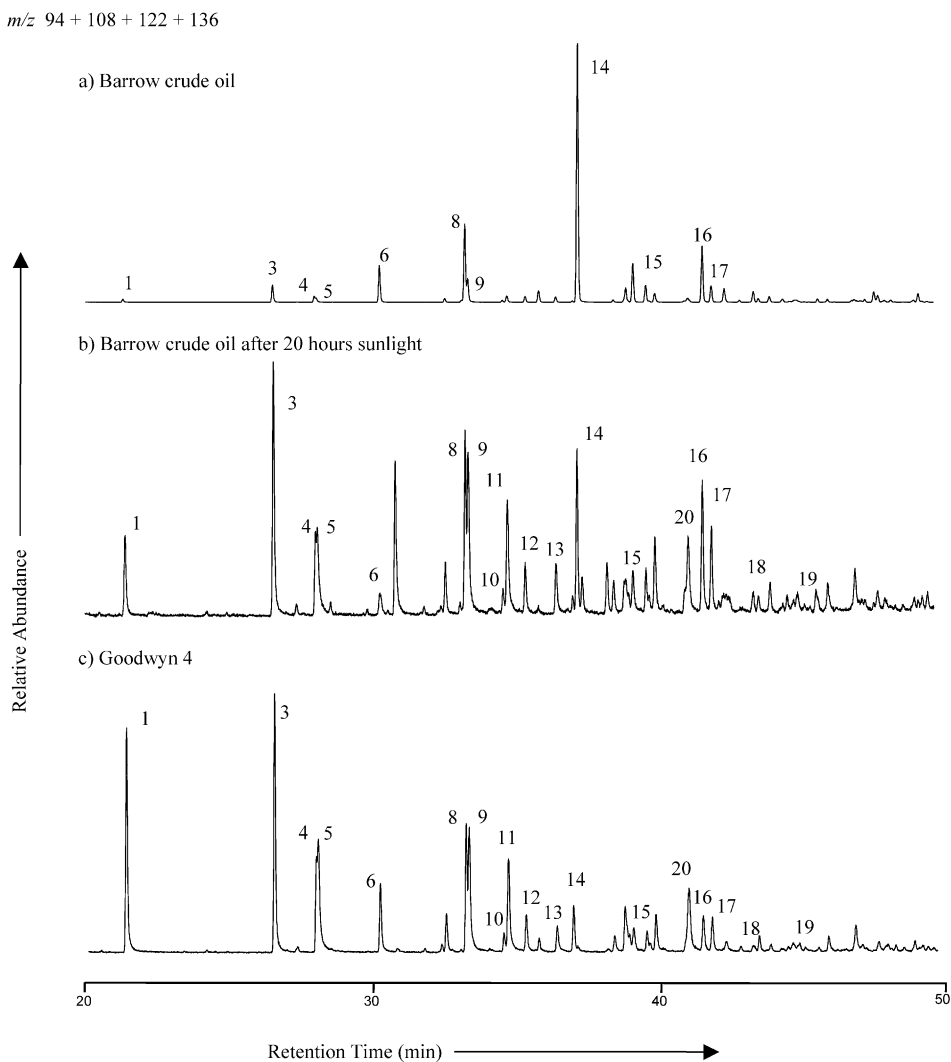


Fig. 3. Partial combined m/z 94 + 108 + 122 + 136 mass chromatograms showing the C₀, C₁, C₂ and C₃ alkylphenol distribution in (a) Barrow crude oil, (b) Barrow crude oil exposed to 20 h sunlight, and (c) Goodwyn condensate. For peak identifications refer to Table 4.

oxidation (Barrow crude oil) and storage (Legendre crude oil) results in an increase of 3,5-dimethylphenol and 3-ethyl-5-methylphenol relative to the total dimethyl- and trimethylphenols respectively.

Alternatively, it could be argued that a similar, although reverse trend could be expected for samples that have experienced water-washing, which would result in a decrease in the proportion of unshielded isomers (Taylor et al., 2001) such as 3,5-dimethylphenol and 3-ethyl-5-methylphenol. It can also be expected that water-washing does not alter the composition of the unshielded isomers significantly. Therefore, if water-washing was a major factor in the variations observed in the alkylphenol distributions the abundance of 3,5-dimethylphenol and 3-ethyl-5-methylphenol relative

to the unshielded C₂ and C₃ alkylphenols, respectively, a linear relation would not be expected. However, if oxidation determines their abundances then a correlation can be expected, because both 3,5-dimethylphenol and 3-ethyl-5-methylphenol are more resistant to oxidation than other unshielded isomers. Fig. 5 shows that there is indeed a significant correlation ($r^2=0.81$) between these parameters, suggesting that the relative abundances of 3,5-dimethylphenol and 3-ethyl-5-methylphenol are more likely to be controlled by oxidation rather than water-washing. Using these parameters a larger variation was observed with the Legendre samples than in Fig. 4, however, this is most likely caused by the low concentration of some isomers, especially 3,4,5-trimethylphenol.

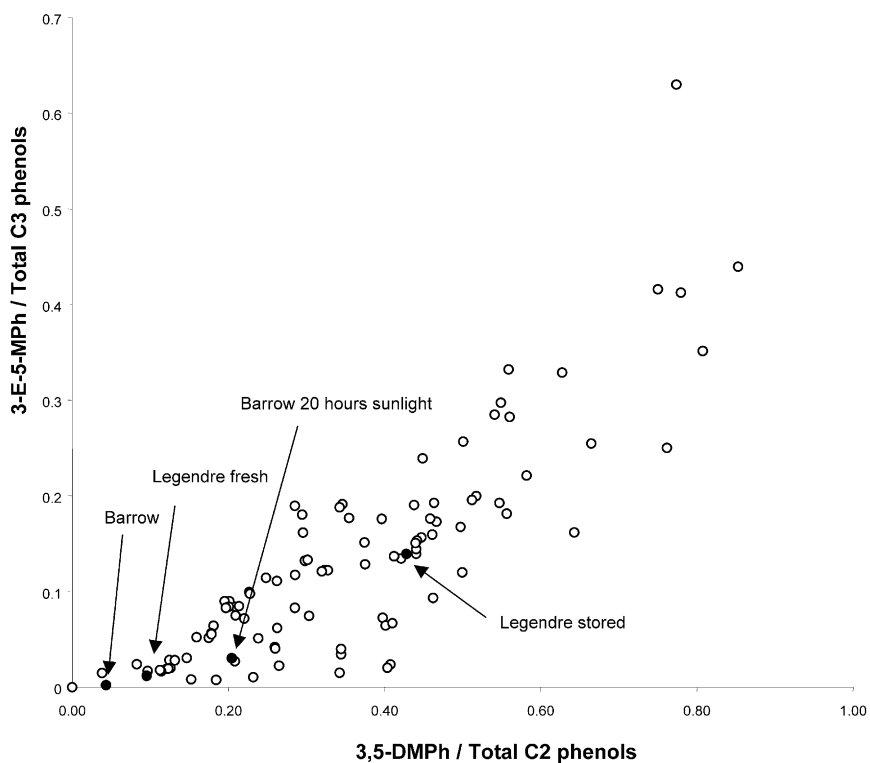


Fig. 4. Plot of 3,5-dimethylphenol/total dimethylphenols versus 3-ethyl-5-methylphenol/total trimethylphenols for 123 crude oils from the Carnarvon Basin.

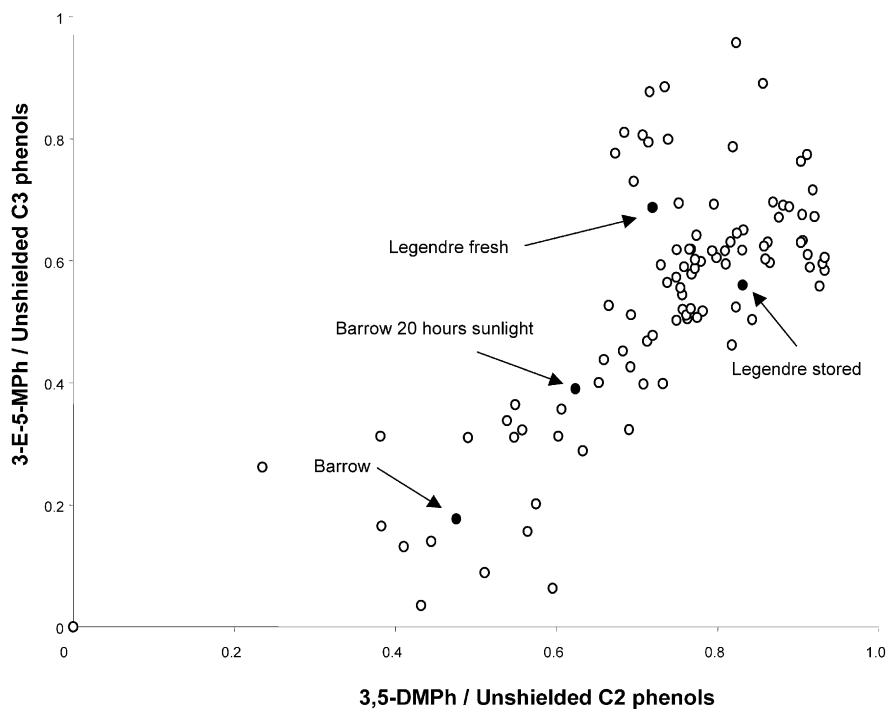


Fig. 5. Plot of 3,5-dimethylphenol/unshielded dimethylphenols versus 3-ethyl-5-methylphenol/unshielded trimethylphenols for 123 crude oils from the Carnarvon Basin.

Table 4
Alkylphenols identified in crude oils and their peak assignments

Peak no.	Compound	Abbreviation
1	Phenol	Ph
2	2-Br-phenol	x-
3	<i>o</i> -Cresol	<i>o</i> -
4	<i>p</i> -Cresol	<i>p</i> -
5	<i>m</i> -Cresol	<i>m</i> -
6	2,6-Dimethylphenol	2,6-DMPH
7	2-Ethylphenol	2-EPh
8	2,4-Dimethylphenol	2,4-DMPH
9	2,5-Dimethylphenol	2,5-DMPH
10	4-Ethylphenol	4-EPh
11	3,5-Dimethylphenol	3,5-DMPH
12	2,3-Dimethylphenol	2,3-DMPH
13	3,4-Dimethylphenol	3,4-DMPH
14	2,4,6-Trimethylphenol	2,4,6-TMPH
15	2,3,6-Trimethylphenol	2,3,6-TMPH
16	2,4,5-Trimethylphenol	2,4,5-TMPH
17	2,3,5-Trimethylphenol	2,3,5-TMPH
18	2,3,4-Trimethylphenol	2,3,4-TMPH
19	3,4,5-Trimethylphenol	3,4,5-TMPH
20	3-Ethyl-5-methylphenol	3-E-5-MPh

Peak numbers refer to Figs. 1–3.

3.5. Factors affecting extent of oxidation

Light enhances the oxidation process but is not essential; the oxidation of phenols can proceed without the inducement of light (Scott, 1993). The impact of light can be avoided by storing samples in opaque containers such as metal tins and drums. However, many factors can come into play and affect the extent of oxidation. These include properties of the crude oil such as its opaqueness, available oxygen, the original concentration of the alkylphenols and the presence and concentration of other more photosensitive compounds. In crude oils with lower concentrations of alkylphenols, their distributions are likely to be affected to a relatively greater extent as the alkylphenols become the limiting reagent in the oxidation reactions.

Other factors involve the storage conditions, such as the amount of sunlight versus artificial light that falls on the sample, the type of container (clear or amber glass) and volume of the air gap in the container. Many of these factors can be overcome by storing larger volumes of crude oil in opaque, air tight containers with little or no air gap and/or flushing the container with an inert gas such as nitrogen or argon just prior to sealing the container.

4. Conclusions

Alkylphenol mixtures and a crude oil exposed to light and air for various periods were altered significantly,

suggesting that the alkylphenol distributions in geochemical samples can be severely altered by exposure to light and air. Oxidation, enhanced by exposure to light, degrades *ortho*- and *para*-substituted isomers, such as 2,4- and 2,6-dimethylphenol and 2,4,6-trimethylphenol more rapidly, whereas phenol, *m*-cresol, 3,5-dimethylphenol and 3-ethyl-5-methylphenol (and 2,5-dimethylphenol in less affected samples) are much more resistant.

Comparison of the alkylphenol distributions of a stored and a fresh crude oil from the same accumulation showed significant differences, consistent with oxidation of the stored sample. Similar alkylphenol distributions were measured in many stored samples, suggesting they too had undergone oxidation. Therefore, care should be taken when interpreting the distribution of alkylphenols because oxidation of alkylphenols during the storage of crude oils could present a significant problem.

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