Use of Short Chained Alkylphenols (SCAP) in Analysis of Transport Behaviour of Oil Contaminated Groundwater

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فينولات الالكايل ذات السلسلة القصيرة في المياه الجوفية الملوثة بالنفط الخام

مارتن سوتير وتوبياس ليشا

خلاصــة: بشــكل فيـنولات الالكـايل مكونـا رئيسـيا للنفط الخام ومنتجات الفحم المسيلة. وتوجد هذه المواد في المياه المصـاحبة لإنـتاج الـنفط والمياه الجوفية الملوثة من التسربات النفطية ومناطق إنتاج النفط والفحم. ولقد تم تطوير تقنية عدديـة مـتطورة للكشـف عن كل المركبات الأربعة والثلاثون لهذه المواد. ويمكن ملاحظة الحركة الانقسامية لهذه المواد في المـياه الجوفية نتـيجة للخـواص الفيزيوكيميائية المخـتلفة لفيـنولات الالكـايل، مغـيرة تركيزها النسـبي مـع الوقت والمسـاحة. ويمكـن الاسـتفادة من هذه الخواص لمعرفة اتجاه حركتها ووهن تركيزها مع الوقت. ودراسة الحالة المقدمة تدل على الاستخدامات العملية لهذه التقنية.

ABSTRACT: Shortchained alkylphenols (SCAP) represent a main constituent of crude oil and coal liquefaction products. Due to their specific oil/water partitioning behaviour and high aqueous solubility they can be detected in oil exploitation waters and groundwaters affected by various spills near oil pipelines, oil exploitation sites and coal liquefaction plants. New efficient and powerful analytical techniques have been developed that allow the identification of all 34 individual compounds (C_0-C_3) without derivatisation and in complex matrices. Due to the different physico-chemical properties of the SCAP, differential transport behaviour in groundwater can be observed, changing the relative concentrations of SCAP downgradient in space and time. These characteristic ratios can be employed to derive information on migration direction and the ageing of the source of contamination. A case study is presented to illustrate the use of this new tool.

Keywords: Alkylphenols, crude oil, groundwater, partioning, plume, biodegration, toxicity, GC-MS, tar oil, anaerobic.

Crude oil consists of a complex mixture of organic compounds. Among those alkylphenols are the main constituents. Depending on the quality and origin of the fossil fuel, the concentrations of the alkylphenols may vary considerably (Taylor *et al.* 1997). Larter and Aplin (1995) suggested employing short chained alkylphenols (SCAP) as indicators for oil quality, the extent of the source and as tracers for the petroleum migration process. The respective technique mainly relies on the specific partitioning behaviour of phenols between the water and oil phase. Taylor *et al.* (1997) and Ioppolo *et al.* (1992) investigated numerous crude oils for their individual SCAP concentrations. They confirmed that SCAP are ubiquitous constituents of crude oil thus making the oil quality and quantity estimation universally applicable. Apart from crude oil, alkylphenols also occur in shale oils and coal liquefaction products (Licha *et al.,* 2002).

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Although phenols can be a very valuable tool in oil exploration, they can become a major problem during oil exploitation. The main wastes of environmental concerns associated with onshore oil and gas production are SCAP contaminated drilling-waste fluids or muds, drilling-waste solids and wastewater. Crude pipelines are routinely cleaned. This can lead to surface oil spills. Wastewater from crude oil processing can contain up to 50 mg/L of SCAP. Probably one of the best documented and researched spill sites of crude oil from a broken pipeline is from Bemidji, Minnesota (USA) (Bekins *et al.,* 2001, Baedecker *et al.,* 1993). At this site the development of the contaminant plume, the organic and inorganic geochemistry as well the microbiology has been investigated for more than 16 years.

In this paper we present techniques for the analysis as well as the employment of SCAP for the characterisation of the contamination source and the associated groundwater contamination plume. We believe that the presence of phenols in the subsurface has largely been underestimated and their biodegradation largely overestimated. Although our main experience stems from sources comprising coal liquefaction products, the principles presented here also apply to contamination from crude oil and oil production waters.

Properties of SCAP and Environmental Relevance

In this section a brief overview on the properties of short chained alkylphenols is given. Particular emphasis is put on those physico-chemical properties that affect their special respective transport behaviour as well as their environmental relevance.

SCAP are phenols for which hydrogen atoms from the benzene ring are substituted by alkyl groups with various chain length. The number of carbon atoms outside the ring is given in the form C_X, where C stands for carbon and x for the number of atoms outside the ring. To clearly separate them from other alkylphenols the abbreviation SCAP is introduced. Short chained alkylphenols are comprised of the following eight groups with their respective isomers. In total, SCAP include 34 short chained alkylphenols (C_1-C_3) and phenol itself (C_0): phenol (C_0), cresols (C_1) with 3 isomers, dimethylphenols (C_2) with 6 isomers, ethylphenols (C_2), with 3 isomers, trimethylphenols (C_3) with 6 isomers, ethyl methylphenols (C_3) with 10 isomers, n-propylphenols (C_3) with 3 isomers, and isopropylphenols (C_3) with 3 isomers. Figure 1 shows structural chemical formula of typical representatives of each of the above groups.

Data on the physical and chemical properties of SCAP are only reported for some isomers. In fact, no data are available for approximately 30% of all the compounds. Therefore their environmental behaviour still remains uncertain.
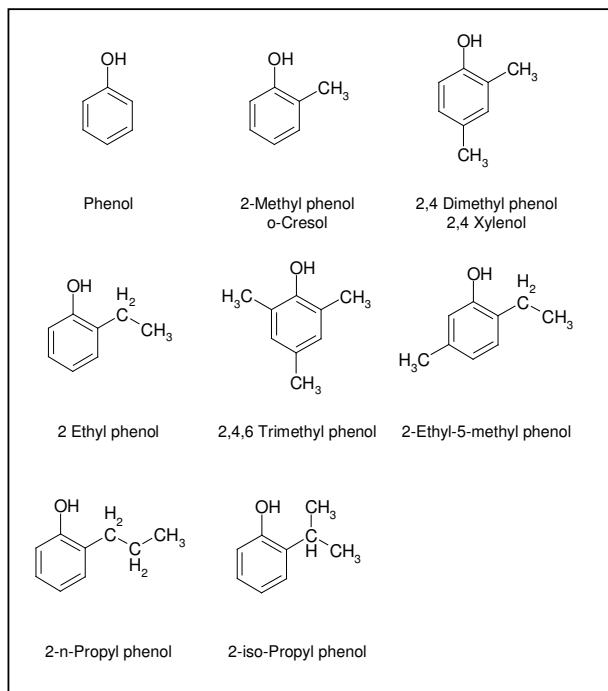

Figure 1. Chemical formula of representatives of each of the eight SCAP subgroups.

SCAP are highly water soluble compounds, with solubilities much higher than other common organic contaminants such as BTEX or PAK and even higher than most inorganic salts. This effect is caused by the ability of SCAP to participate in hydrogen bridging bond systems. The hydroxyl group in phenols forms this electrostatic bond with water molecules. If the hydroxyl group is blocked by a substituent in ortho-position (like 2-ethylphenol) the solubility should decrease. Bennett and Larter (1997) described this solubility influence of substituents based on oil-brine partitioning experiments. Solubility data obtained by Varhanickova *et al.* (1995) show a different behaviour. The solubility in their investigation varied between that of the individual compounds and decreases from C_0 to C_2 by approximately two orders of magnitude. The solubilities determined by Varhanickova *et al.* (1995) under identical conditions (i.e. concise set of data) are presented in Table 1. The reported high solubilities are the main reason for their high concentrations in groundwater, the large travel distances and a large variation in solubilities of the individual SCAP together with the differential transport behaviour of SCAP, outlined below.

Further, SCAP are weak acids, due to the deprotonation ability of the hydroxyl group in aqueous solutions. However, a significant deprotonation only occurs at pH values well above 8. This is because the acidity constants (pK_a) for the individual isomers range between 9.9 and 11 (Taylor *et al.,* 1997). Thus, SCAP are in groundwater almost always in undissociated/protonated form. SCAP are

TABLE 1

Solubilities of SCAP compounds at 25°C (Varhanickova et al., 1995).

Compound	Solubility (g/L)	Compound	Solubility (g/L)
Phenol	102.1	3,5-Dimethylphenol	6.7
o-Cresol	26.8	2-Ethylphenol	14.0
m-Cresol	19.6	4-Ethylphenol	8.0
p-Cresol	22.0	2,3,5-Trimethylphenol	0.9
2,3-Dimethylphenol	6.4	2,4,6-Trimethylphenol	1.4
2,4-Dimethylphenol	8.2	3,4,5-Trimethylphenol	1.5
2,5-Dimethylphenol	3.8	4-nPropylphenol	1.3
2,6-Dimethylphenol	6.2	2-isoPropylphenol	4.4
3,4-Dimethylphenol	7.2	4-isoPropylphenol	3.3

as soluble as ions but do not carry a charge in groundwater. They do not participate in ion exchange, neither do they occur as a pure phase unlike LNAPLs or DNAPLs. This raises the question to what extent common theories and general principles regarding transport behaviour derived from either insoluble organic compounds or ionic compounds may apply to organic substances readily soluble in water.

Since SCAP toxicity with respect to the human body cannot be specified yet in detail, analogies must be applied from data gained in microbial tests and from known cresol toxicities. Some individual SCAP have been investigated for their toxicity with Toxkit microbiotests, 15 minutes EC 50 (Kahru *et al.,* 1999). According to these tests, the toxicity increases in the sequence C_0-C_1-C_2. This may be a result of the different metabolic pathways, increased lipophilic character and an increased residence time in the organism. The effect on humans, however, may be entirely different, presumably much less. SCAP are toxic for aquatic organisms; an environmental concern level of 0.02 µg/L can be determined by applying the modified US EPA method. Adequate data on plants and terrestrial organisms are lacking. Based on the above environmental concern level for water, it is reasonable to assume that aquatic organisms may be at risk in any surface or sea water contaminated with phenol. Their toxicity threshold values are orders of magnitude lower than their solubilities. This fact must be of main concern when dealing with phenol contamination. The available data are summarised in Table 2. It is apparent from this table that the degree of toxicity increases considerably for cresols and dimethylphenols.

Chemical Analysis of SCAP

A number of methods for the analysis of individual phenols have been published. A summary of those has been given by Möder (2000) and Lüders (1999). These include: liquid chromatography, gas chromatography and capillary zone electrophoresis. Depending on the separation technique and the sample type, various sample preparation methods and detection systems were suggested. All procedures require a substantial effort in sample preparation in order to obtain a full separation of all 35 SCAP. The nearly full separation of all SCAP by GC-MS without the elaborate derivatisation step has not yet been described. In order to investigate and economically monitor those phenols in the environment, the development of a precise, robust and cost effective analytical technique has been developed by the authors. This analytical method takes advantage of the latest and commonly established developments in sample preparation and gas chromatography column technique. The solvent free extraction technique SPME offers an easy way of enrichment from environmental samples. This technique has so far been successfully applied to EPA phenols by Buchholz and Pawliszyn (1993; 1994). SPME could be shown as successful for the analysis of chloro- and nitrophenols even from complex matrices using a polyacrylate fibre (Möder *et al.*, 1997). The use of cyclodextrine based capillary columns in the gas chromatographic separation has been reported to be an excellent stationary phase to separate not only enantiomers but also positional isomers. In the following, the method is described in more detail.

Phenol standards were purchased from Dr Ehrendorfer as Phenol Mix 1, containing 50ng/µl of each compound (phenol, 3 cresols, 6 dimethyl phenols and 4 trimethyl phenols). The 3 ethyl phenols and 5 propylphenols were purchased from Fluka. The internal standard d3-2,4 dimethyl phenol was supplied by Promochem.

SPME Conditions

The polyacrylate SPME fibre (PA of 85-µm coating) was supplied by Supelco. The sample was extracted from headspace (headspace SPME, HS-SPME), which requires the following sample preparation steps to yield maximum sensitity. A volume of 10 ml aqueous sample was placed in a 22 ml headspace vial containing 2.5 g of

TABLE 2

Toxicity of SCAP.

Compound	Toxicity (mg/l)	Compound	Toxicity (mg/l)
Phenol	97.3	2,3-dimethylphenol	41.2
o-cresol	51.8	2,6-dimethylphenol	29.0
m-cresol	83.8	3,4-dimethylphenol	6.1
p-cresol	7.7		

Toxkit microbiotests data from Kahru *et al.* (1999).

NaSO$_4$. This mixture was spiked with 5 µl internal standard and 5 drops of H$_2$SO$_4$ (96% p.A.) were added, sealed immediately and placed into the auto sampler rack. Prior to the extraction step each vial was automatically agitated at 50°C for 10 min. The HS-SPME was then carried out at 50°C for 45 min. Finally, the analytes were thermally desorbed in the split/splitless injector port of the GC at 280°C for 3 min with a splitless time of 60 s.

GC-MS Method

A Hewlett Packard GC-MS instrument (GC: 6890, MSD: HP5972A) was used in combination with a Combi-PAL auto sampler (CTC Analytics) to perform the SPME step and the following analysis automatically and simultaneously. An capillary column with an inclusion dominated separation property (α-DEX 120 (Supelco), 60 m × 0.25 mm I.D., 0.25 µm film thickness) was applied. Helium flow rate was set at 1.8 ml/min. The GC oven program started at 50°C. The initial temperature was held for 3 minutes and was then increased at a rate of 7°C/min to 136°C. After an isothermal period of 2 minutes a temperature gradient of only 0.4°C/min was applied until 142°C was reached and held for another minute. A final ramp of 8°C/min up to a temperature of 215°C and finally held for 7 minutes end the run. Consequently, each analysis requires 60 minutes. The simultaneous extraction and GC separation allows the analysis of 24 samples per day. The following separation for some selected SCAP is shown on a real sample in Figure 2.

The inclusion mechanism existing in cyclodextrin based capillary columns shows excellent selectivity for positional isomers of SCAP and allows their underivatised analysis in samples with complex matrices by maintaining a high separation efficiency combined with a very good sensitivity. Unfortunately, the performance of such columns drops sharply in the presence of water traces. To overcome this drawback and significantly extend the life time of the column a selective virtually water free sample preparation technique was chosen in exposing the SPME-fibre to the headspace of the sample. Additionally, HS-SPME limits the amount of analyte introduced to the column, which itself has due to the added cyclodextrin a very low analyte capacity. Thus, HS-SPME improves results, increases life time of the fibre and the capillary column and enables an economical application of this combined technique to a wide variety of samples. Achievable detection limits using a polyacrylate SPME fibre are 0.5, 0.3, 0.2, and 0.1 µg/l for C$_0$, C$_1$, C$_2$ and C$_3$ SCAP, respectively. By using ring deuterated 2,4-dimethylphenol as the internal standard a high reproducibility is ensured. Simultaneously, internal standardisation allows an evaluation of the influence of dissolved organic matter. Several studies confirm this approach (Pörschmann *et al.*, 1998).

Conceptual Model of Differential Transport of SCAP

The above described different physical and chemical properties of SCAP, together with the respective differences in their adsorption behaviour implies differences in the spreading of the individual SCAP and therefore a change in their relative composition. Furthermore, the source composition will change as well as a result of the differential depletion in the various compounds with time.
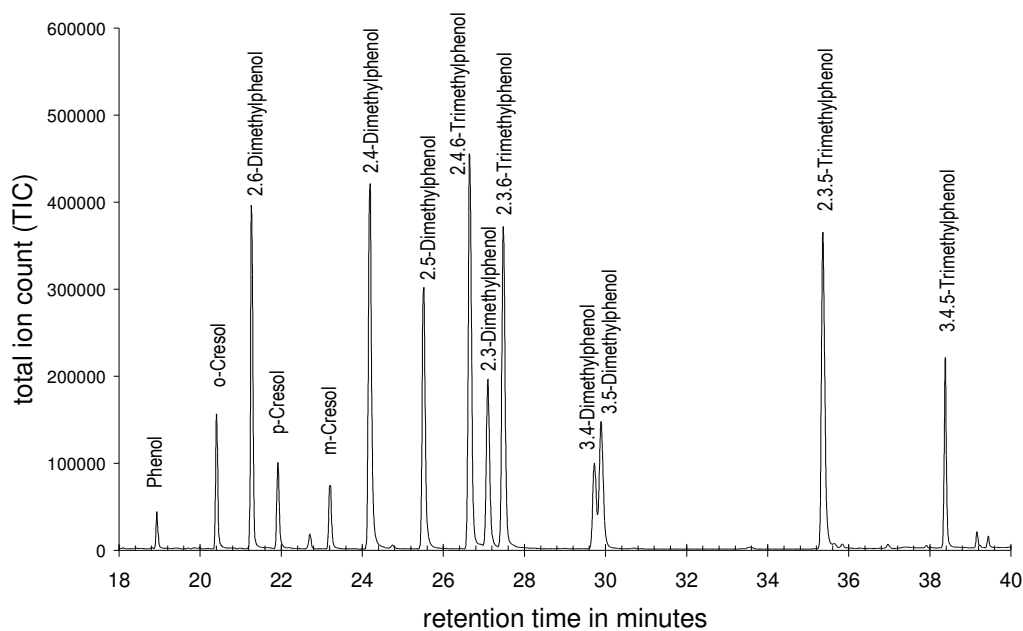

Figure 2. Chromatogram of 14 SCAP, each 10 µg/L in tar matrix (SIM-MODE).

The chemical analytical technique allows a refined investigation of SCAP in water and sediments at contaminated sites. A transport parameter, derived from site and laboratory investigations, is suggested to account for the different adsorption data existing for the individual SCAP. Generally, the more carbon atoms outside the benzene ring, the stronger these SCAP are retarded. From our experiments a factor of 10-50 for the Freundlich coefficient between C_0 and C_3 SCAP was determined for sand/subbituminous coal. This partitioning parameter is termed phenol-cresol-fraction, abbreviated as PCF and defined as:

$$PCF = \frac{M_{Phenol}[mmol/L] + M_{Cresols}[mmol/L]}{\sum M_{SCAP}[mmol/L]}$$

The PCF can take on a value between 0 and 1. A total SCAP concentration of 0.0 mmol/L has no PCF by definition. PCF variations are caused by surface processes. Thus, travel velocity, travel time, travel distance and surface properties are the most sensitive parameters to cause this variation. PCF values across a SCAP contaminated site can be used as partitioning tracers. They can furthermore indicate the type of source from where the SCAP originate (Table 3). From the SCAP distribution at the site, groundwater flow and contaminant transport direction, the type (Table 2) and age of contamination (Figure 4-6) can be derived. The presence of organic matter in the aquifer leads to a further separation of the different SCAP resulting in a continuing enrichment of the plume's tip with respect to the easily soluble and little retarded C_0-C_1 SCAP compounds. Table 3 summarizes PCF-values gained from our field investigations.

TABLE 3

PCF variation with source, time and space.

Anaerobic	Input	Ageing Source	Tip of Plume
LTC plant waters	0.75-0.85	0.30-0.60	0.90-1.00
Tar contamination	0.20-0.30	0.00-0.15	0.40-0.65

The PCF, however, can only be successfully applied if it is not superimposed by other processes such as degradation, which is usually the case in anaerobic conditions. The SCAP differentiation across a plume and its development over time can be expressed by the PCF. Figures 3 to 5 show a conceptual model for source and plume development for three different scenarios. Water equilibrated with crude oil (PCF 0.8) is assumed as the SCAP source in all three scenarios. Crude oil itself has a PCF of 0.5 but since C_0-C_1 -SCAP are much easier soluble in water, their proportion rises in the equilibrated water to a PCF of 0.8.

Figure 3 shows the influence of the presence of natural organic matter (NOM) on SCAP differentiation. A PCF variation is only observed if retardation can be assumed. Since C_0 is virtually unretarded, the plume length is not greatly affected by the presence of NOM. The percentage, distribution and type of NOM in the aquifer together with the water velocity and the kinetics of the adsorption determine the degree of differentiation. From a continuously supplying source with a PCF of 0.8 a total variation in the range between 0.8 and 1.0 can be observed.
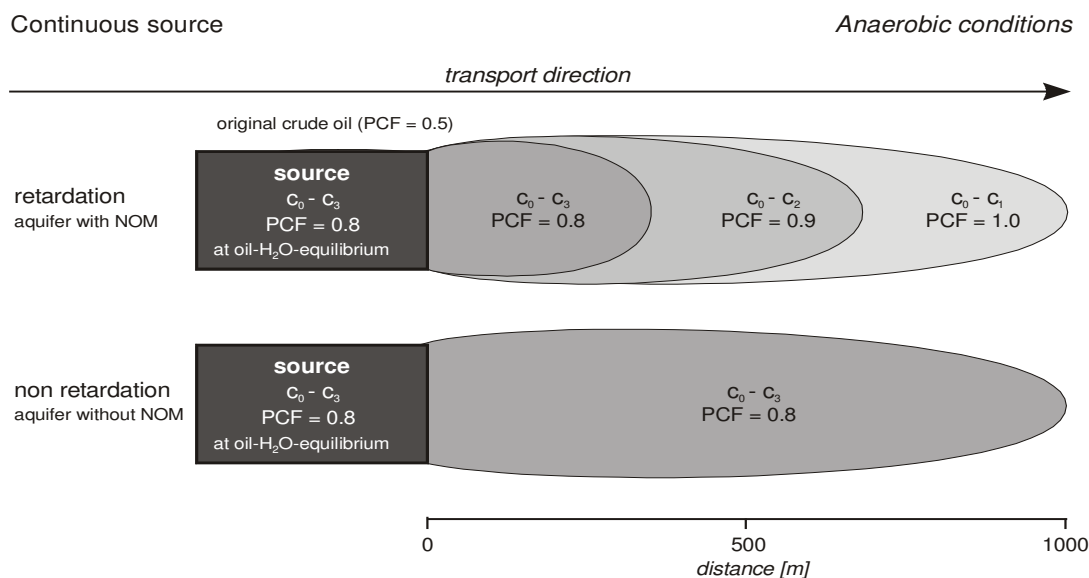

Figure 3. PCF variation with and without retardation.

Gradually depleting source

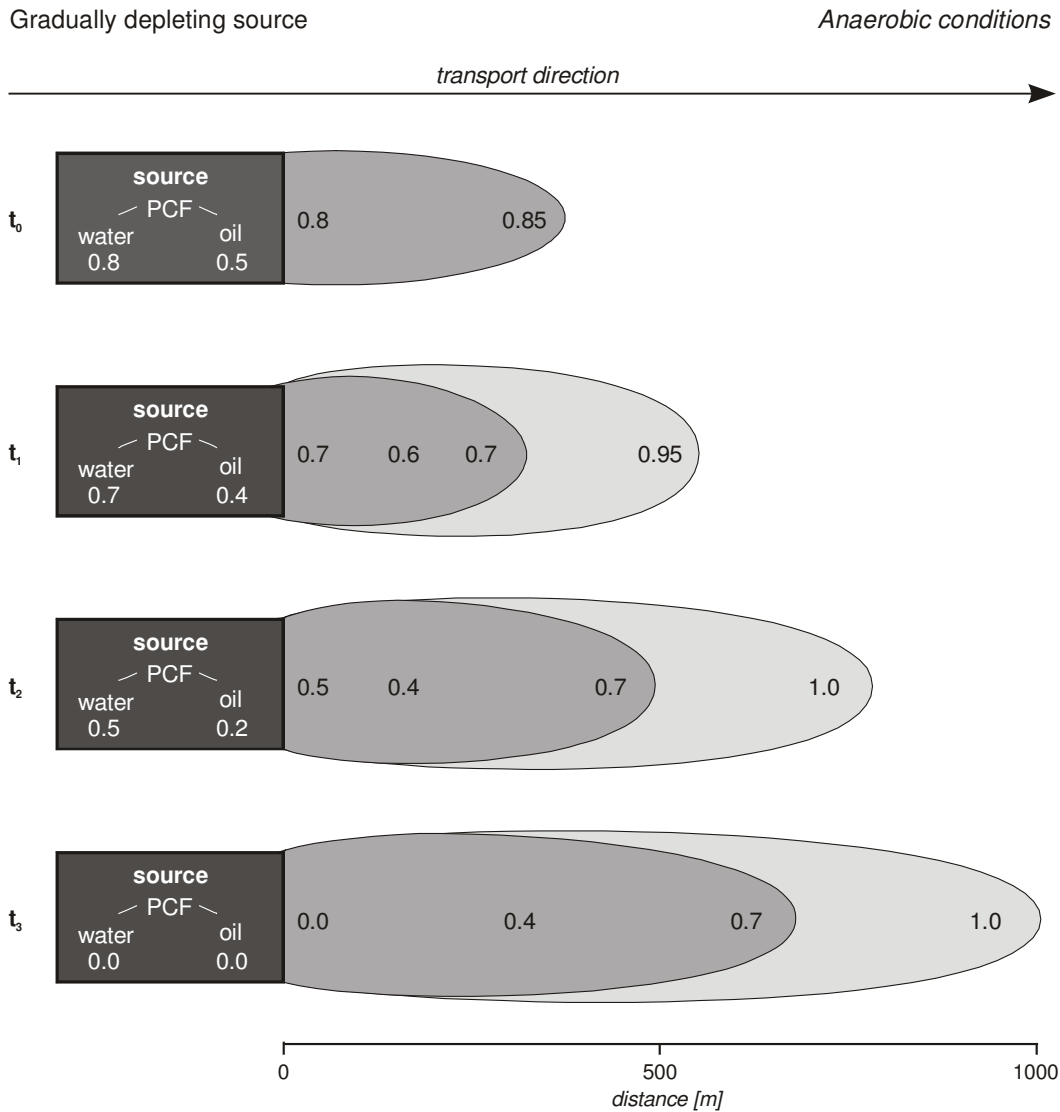*Anaerobic conditions*

transport direction

Figure 4. Temporal change in PCF in a plume from a gradually depleting source.

A gradually depleting source as shown in Figure 4 does not have a constant PCF over time. The source gets more rapidly depleted with respect to the highly soluble C_0 and C_1-SCAP while the less soluble C_2 and C_3-SCAP remain longer in the source zone. Therefore, the PCF in the source gradually decreases and in some cases may even reach zero. A PCF of 0 means that no C_1-C_0 SCAP are present. It does not give any information on how much C_2-C_3 SCAP remains, nor does it indicate a total SCAP concentration of zero. A decreasing PCF of the source gradually changes the boundary condition. It is therefore difficult to illustrate the development of the plume without numerical modelling. The PCF variation across the plume simultaneously increases until it eventually covers the whole range of PCF starting with 0 at the source and finishing with a value of 1 at the tip of the plume. The same, but much faster effect on the PCF, is obtained if the contamination is small and if the source disappears completely, i.e. a pulse input (Figure 5).

The onset of the plume is being continuously depleted with respect to the non retarded C_0-C_1 by the flushing effect of uncontaminated groundwater. Again, the PCF variation as well as the extent of the plume depend on the groundwater velocity; the extent, type and distribution of NOM in the aquifer system and the travel time.

Pulsed input

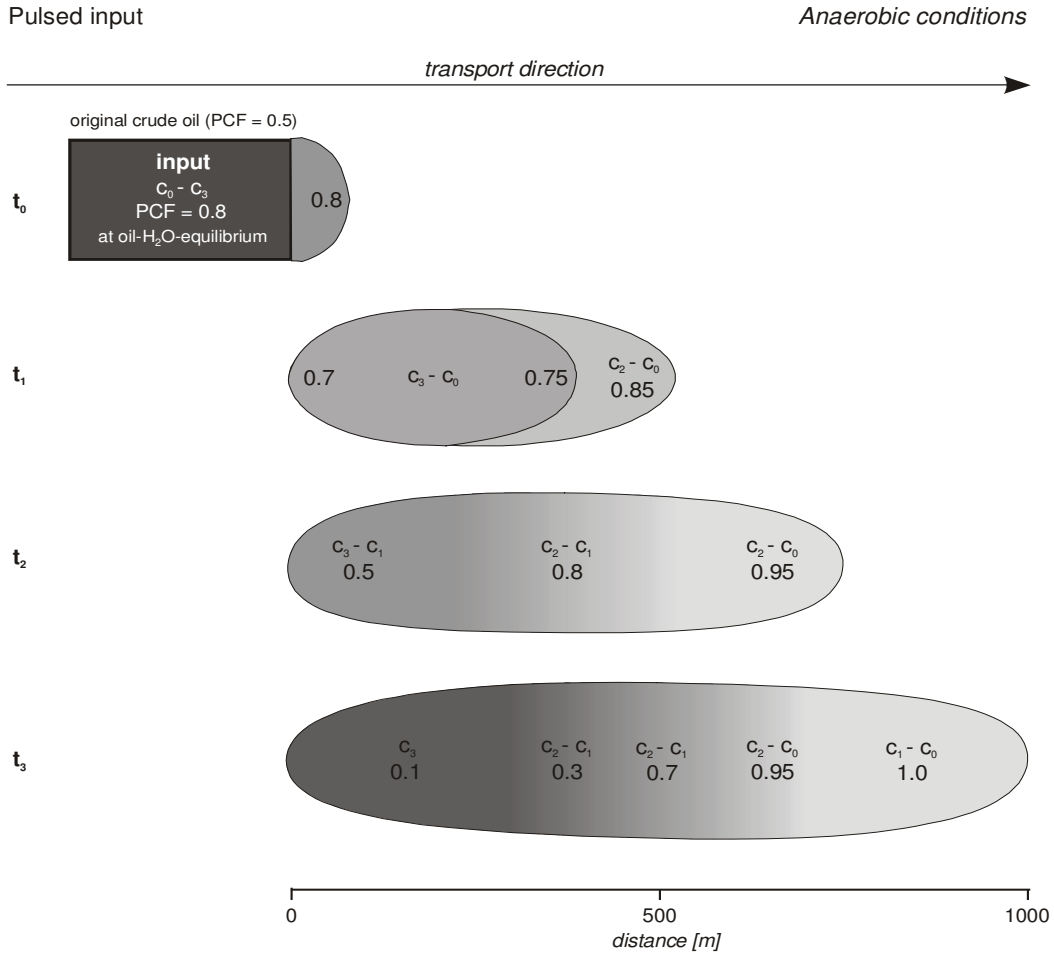*Anaerobic conditions*

transport direction

Figure 5. PCF change in the plume from a short lived source.

Figure 6 summarises observable PCF-values in a tar oil contaminant plume depending on distance from the source and age of the source. The plot is a synthesis of theoretical considerations and field observations. The straight lines in the plot are only schematic. The relationship may not necessarily be linear.

Field Investigation of a Subsurface Tar Oil Contamination

In order to illustrate SCAP transport in a real aquifer and to demonstrate the potential value of SCAP for the assessment of the contamination potential, initial results for tar oil contaminated groundwater are presented.

The site is on the premises of a former gas works which was in operation until the early 1990s producing town gas from subbituminous coal. The study area is 50,000 m^2 (200 by 250 m) and located adjacent to a river. Alluvial deposits such as gravel and sand dominate the contaminated subsurface aquifer. The water table is shallow (1.5 m to 3 m below ground level), the aquifer slightly confined, highly transmissive with a hydraulic conductivity of 1.4 10^{-4} m/s and a groundwater velocities
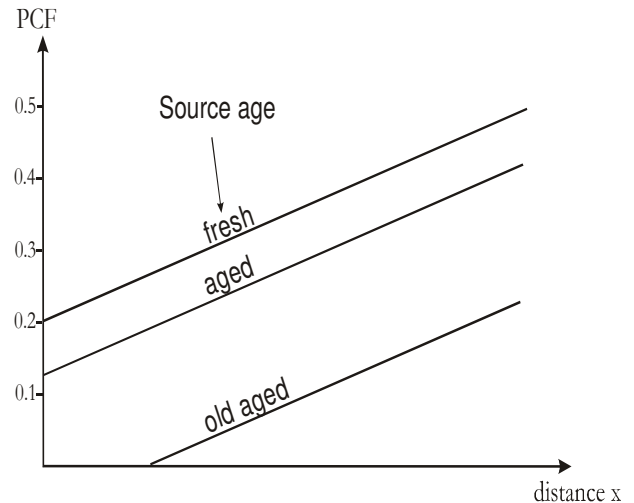

Figure 6. PCF variation across a tar contaminated site over time.

of up to 1 m/d. Groundwater flow direction is NNW to SSE.

SCAP contamination was found near a tar pit source and along the assumed groundwater flow path (Figure 7). First sampling (11/2001) took place after an extended dry
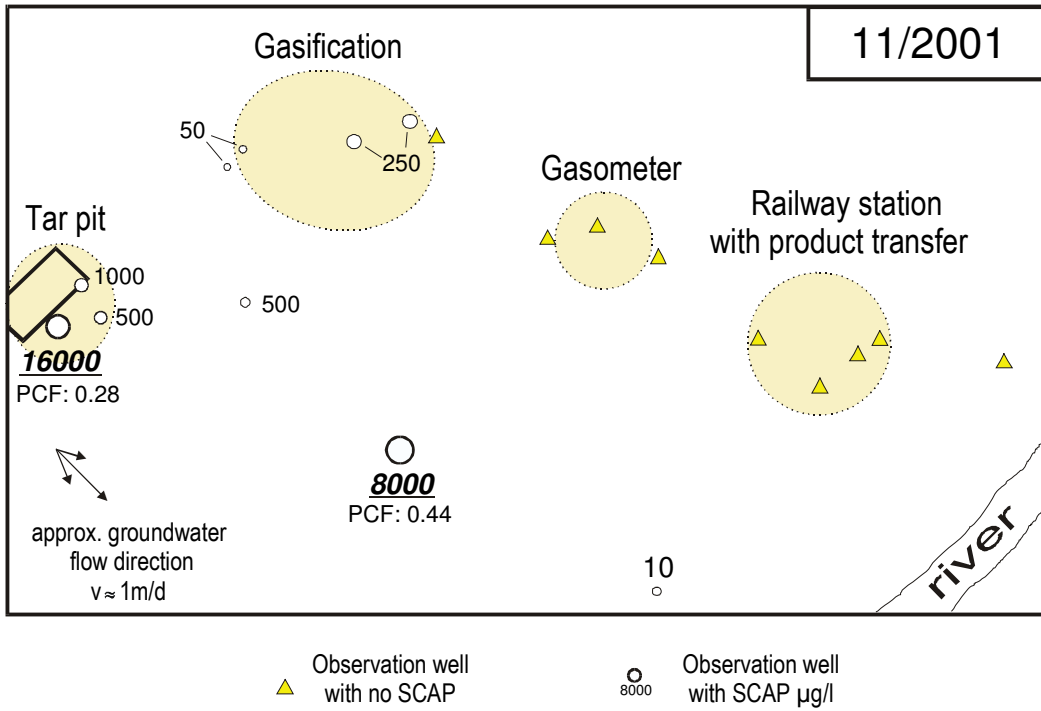
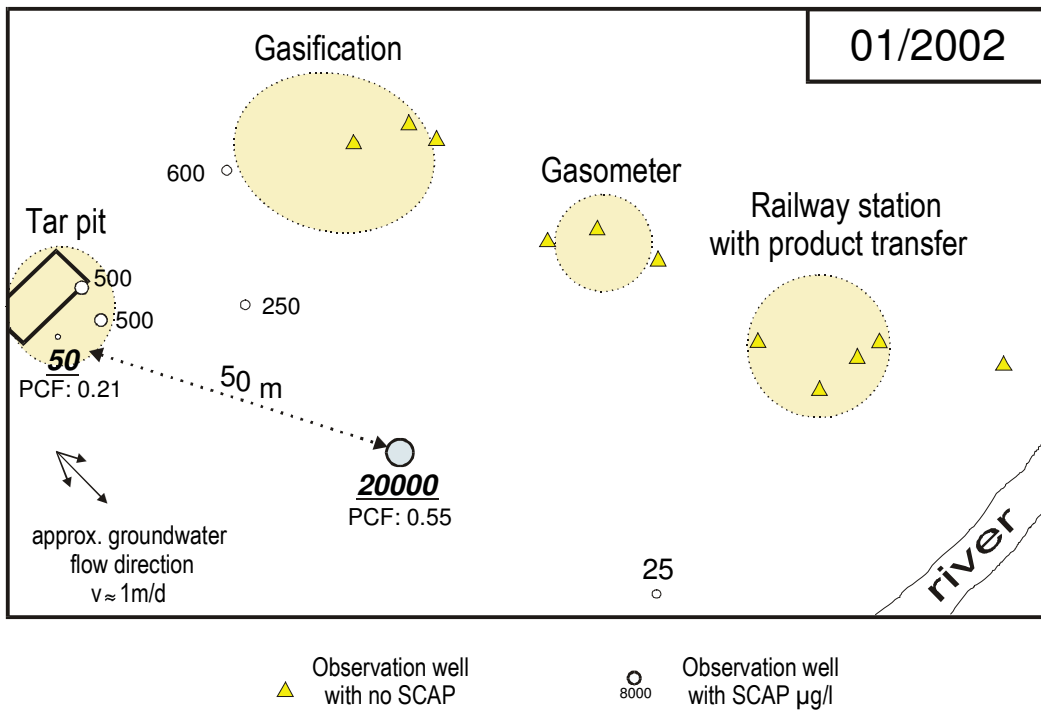**Figure 7a**. Shallow SCAP contamination (µg/L) at a gasworks site after a long dry period.

Figure 7b. Shallow SCAP contamination (µg/L) at a gasworks site after a rainfall period.

period (Figure 7a). The highest SCAP concentration was found at the tar pit with 16,000 µg/L with a PCF of 0.28. Groundwater abstracted from an observation well 50 m downgradient of the tar pit was highly contaminated. The PCF in this well was 0.44. This indicated enrichment in C_0/C_1 SCAP relative to that of the tar pit which showed a PCF as expected from typical tar contamination. The second sampling (01/2002) was carried out after a 2 month period with numerous rainstorm events (Figure 7b). The highest SCAP concentration was now measured at the downstream well of 20,000 µg/l. This was an even higher concentration than that observed at the tar pit two months previously. Simultaneously, the SCAP concentration at the source well near the tar pit had dropped to only 50 µg/L which approximates the target value for remediation. Assuming that SCAP easily dissolve in the new recharge water in the area of the tar pit and with a groundwater velocity of 1 m/d it can be concluded that the water sampled in the observation well represented the recharge water that flushed the source 60 days earlier. The PCF at the tar pit dropped to 0.21 within these 60 days while the PCF at the observation well increased to 0.55.

In summary, these findings indicate that C_0-C_1 SCAP can travel more or less unretarded. SCAP can be easily flushed from the source under the present hydrogeological conditions. One can further assume, that the dissolution process of SCAP from tar is slow compared to the intensive flushing during a recharge period. This implies large uncertainties in the prediction of the temporal and spatial distribution of SCAP contamination.

Conclusions

Alkylphenols (SCAP) have been somewhat neglected as a group of contaminants in the past. This is mainly due to the general belief that phenols are highly soluble and therefore easily biodegraded. Our experience shows that they are available in large concentrations in crude oil and tar oil contaminated sites, and that they can travel in groundwater almost unretarded under anaerobic conditions for large distances. We developed techniques that allow for a rapid and accurate quantification of SCAP even in complex matrices in order to assess the extent of the plume. It could further be demonstrated that SCAP can offer a large potential in the identification and characterisation of a source as well as providing a tool to characterise the development stage of a plume if relative concentrations of phenols are determined along the groundwater flow direction.

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