Short chained alkyl phenols (SCAP)

a process orientated tracer for identification of natural attenuation potential

T. Licha, M. Sauter
SCAP- members

- **C0** Phenol (1)
- **C1** Cresols (3)
- **C2** Dimethylphenols (6) Ethylphenols (3)
- **C3** Trimethylphenols (6) Ethyl-Methylphenols (10) Propylphenols (6)

= 19 Compounds
Properties of SCAP

⇒ toxicity (µg/l) increases from C0 to C3
⇒ readily soluble in water (1-100 g/l @ 20°C)
⇒ present in large concentration range (10^8)
⇒ K\text{ow} low (2...10)
⇒ retardation low (R= 1.05…4)
⇒ weak acids (pH controlled behaviour possible)
⇒ degradation behaviour different
⇒ most SCAP degradable under aerobic conditions
⇒ C2-C3 SCAP mostly stable under reducing conditions
  (however-often unknown in the field)
Sources of SCAP

- Carbochemical Industry
  - Cooking plants
  - Carbonisation plants
  - Gasworks sites
  - Tar processing plants

- Petrolchemical Industry
  - Crude oil exploitation
  - Pipelines
  - Petrol production & Petrol stations

= widespread contaminants
SCAP vs. TOC in LTC-waters

**Hirschfelde**
- SCAP: 44%
- Fatty acids: 28%
- Other C-org: 28%

**Espenhain**
- SCAP: 38%
- Fatty acids: 24%
- Other C-org: 38%
Why SCAP as Tracers?

Compounds with:

- common occurrence
- high mobility (SCAP may describe the maximum extend of the organic plume within the aquifer)
- similar but still different enough transport principles
- widespread
- averaging/integral long term signal
- source born!

similar to yesterdays talk on phenoxyacid herbices (P.L. Bjerg)
Sites investigation report

- LTC plants/sites (4)
- Gasworks sites (4)
- Tarprocessing sites (2)
- miscellaneous (2)

- Lignite (7)
- Anthracite (2)
- Tar (1)
- Tar oil (products) (2)

10 positive
2 negative
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LC-Chromatogramm

C₀-C₁  C₂-C₃

ACN 100%: 23.0 %
Flow: 0.40 ml/min
PCF concept

based on molar compound ratios

PCF = \frac{M_{\text{Phenol}} + M_{\text{Cresols}}}{\sum M_{\text{SCAP}}}

PCF: Phenol Cresols Fraction

K_d: C0-C1 < C2-C3
PCF concept

Large concentration range possible - requires knowledge on adsorption mechanism for NA-prediction!
The surface excess problem

\[ n_2^{\sigma(V)} = V^0 \left( c_2^0 - c_2 \right) = V^0 \Delta_{ads} c_2 \]

- \( n_2^{\sigma(V)} \): excess amount of the preferential adsorbed solute 2
- \( V^0 \): the liquid volume
- \( c_2^0 \): starting concentration
- \( c_2 \): concentration in the liquid phase at equilibrium
The surface excess problem

\[ \Gamma_2^{(V)} = \frac{n_2^{\sigma(V)}}{m_A} \]

- \( n_2^{\sigma(V)} \) excess amount of the preferential adsorbed solute 2
- \( \Gamma_2^{(V)} \) surface excess
- \( m_A \) adsorbent mass

\[ \Gamma_2^{(V)} = c_s ? \]
The surface excess problem

\[ n_2^s = n_2^{\sigma(v)} + V^s c_2 \]

- \( n_2^s \) total adsorbed amount
- \( n_2^{\sigma(v)} \) excess amount adsorbed
- \( V^s \) Volume of surface layer
- \( c_2 \) concentration at equilibrium in liquid phase

Kiselev & Shcherbakova (1946)
The surface excess problem

![Graph showing the relationship between log \(c_w\) [µg/l] and surface excess \(\Gamma^{(V)}_2\) (µg/kg).]
The surface excess problem
Adsorption mechanism of SCAP

Adsorption isotherme 11°C für 3,4 Dimethylphenol, pH8, l=0,2
an Sand/Braunkohle (99,5/0,5) (wt%/wt%)

Log $c_s$ vs Log $c_w$

$K_{fr}$ 3
$y = 1.0398x + 0.2132$
$R^2 = 0.9865$

$K_{fr}$ 41
$y = 0.8784x + 0.4816$
$R^2 = 0.8578$

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Adsorption mechanism of SCAP

A

Molecular orientation at low phenol concentrations (1-1000 µg/L)

B

Molecular orientation at high phenol concentration (well beyond 1000 µg/L)
Adsorption mechanism of SCAP

Adsorption isotherme 11°C für 3,4 Dimethylphenol, pH8, l=0,2 an Sand/Braunkohle (99.5/0.5) (wt%/wt%)

- Monomolecular coverage: 2.5 times
- Coverage: 0

Log cs vs. Log cw

- Linear regression equations:
  - y = 0.8784x - 0.4816
  - R² = 0.8578
  - y = 1.0398x - 0.2132
  - R² = 0.9865
  - y = 1.056x + 0.4139
  - R² = 0.9758
  - y = 0.6166x + 1.3786
  - R² = 0.9343
Adsorption mechanism of SCAP

Hemimicell

London Interaction

Hydrogen bonding

London Interaction

ORGANIC MATTER
Sand/Lignite vs. Dolomite

- 3,4-Dimethylphenol onto Lignite/Sand
- 2,6-Dimethylphenol onto Dolomite II
Dolomite

log $\Gamma_2^v$ (nmol/kg) vs. log $c_2$ (nmol/l)

- Phenol
- o-Cresol
- 2,4-Dimethylphenol
- 2,6-Dimethylphenol
- 2,4,6-Trimethylphenol
**Total adsorbed amount**

- Phenol
- o-Cresol
- 2,4-Dimethylphenol
- 2,6-Dimethylphenol
- 2,4,6-Trimethylphenol

**Graphical Data:**
- Log \( \Gamma_2 \) (nmol/kg) vs. Log \( c_2 \) (nmol/l)
- Key markers:
  - 19 Å²
  - 28 Å²
  - 28.5 Å²
  - 36 Å²
  - 36 Å²

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Mechanism

log $\Gamma_2^v$ (nmol/kg) vs. log $c_2/S$

- Phenol
- o-Cresol
- 2,4-Dimethylphenol
- 2,6-Dimethylphenol
- 2,4,6-Trimethylphenol

Non-orientated vs. orientated
Excess isotherm, 3.4DMP, 11°C, pH8, Sand/Coal (99.5/0.5 %wt/wt)

later referred to as Freundlich approximation
1-D Transport model

- Ideal tracer
- 38.5 mg/l (F)
- 100 mg/l (F)
- 250 mg/l (F)
- 38.5 mg/l (P)
- 100 mg/l (P)
- 250 mg/l (P)
1-D Transport model

Retardation factor vs. concentration in mg/L for different isotherms:
- Freundlich Approx
- Phenol steplike Isotherm

First step:
- Retardation factor decreases significantly with increasing concentration.

Second step:
- Retardation factor continues to decrease but at a slower rate compared to the first step.
### PCF-Concept

<table>
<thead>
<tr>
<th>ANAEROBIC</th>
<th>Input</th>
<th>Ageing source</th>
<th>Tip of the plume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonisation plant waters</td>
<td>0.75-0.85</td>
<td>0.30-0.60</td>
<td>0.90-1.00</td>
</tr>
<tr>
<td>Tar contamination</td>
<td>0.20-0.30</td>
<td>0.00-0.15</td>
<td>0.40-0.65</td>
</tr>
</tbody>
</table>
Gradually depleting source

**Anaerobic conditions**

No Degradation allowed
Pulsed input

**transport direction**

original crude oil (PCF = 0.5)

- **input**
  - $c_0 - c_3$
  - PCF = 0.8
  - at oil-H_2O-equilibrium

**Anaerobic conditions**

No Degradation allowed
Anaerobic Transport, NO DEGRADATION

![Diagram showing PCF over travel distance with time points t1, t2, and t3]

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PCF – shallow contamination
SCAP in water

Observation well
with no SCAP

Observation well
with SCAP µg/l

approx. groundwater
flow direction
v ≈ 1 m/d

PCF: 0.21
PCF: 0.28

20000
PCF: 0.55
PCF: 0.44

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Degradation of phenol & cresols allowed

Flow distance x in meters

PCF

no degradation  degradation

SCAP plume from LTC water

SCAP plume from tar source
Quaternary Aquifer, TVW Rositz

Traveltime: appr. 30 years

Traveltime: appr. 1 year
Quartär/Auffüllung  Grundwasserstauer  Braunkohleflöz  Rotliegendes  Grundwasserleiter  Buntsandstein

Flöz II/III
GWL 2/6
Fließrichtung QGWL
S/SE

lokaler GWL

GWL 5/6
Fließrichtung TGWL
N/NW

Werksgelände

Schadstofftransport
durch hydraulischen
Kontakt
(kein direkter Eintrag)

teertypischer
Schadstoffeintrag

Entfernung [m]

100 m

Höhe [m ü NN]
C₂ 98%!

Retardation

C₃

C₂ 77%, C₃ 23%

Degradation  Retardation
C₀ & C₁  C₃

C₀ 22%, C₁ 38%, C₂ 11%, C₃ 29%
p-cresol und m-cresol have almost identical physicochemical properties

under aerobic conditions: different degradation

$$\frac{[m\text{-Cresol}]}{[p\text{-Cresol}]}$$

MPR: Meta Para Ratio

MPR-Concept
MPR- deep injection of LTC waters
SCAP in aquifer material

![Graph showing concentration of o-Kresol, p-Kresol, and m-Kresol](graph)

- o-Kresol
- p-Kresol
- m-Kresol

Konzentration in µg/kg vs. Teufe in m uROK

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MPR- deep injection of LTC waters

SCAP in aquifer material

Teufe in µROK vs. MPR
Summary

- SCAP can be used as reactive Tracers since they are highly soluble (mobil), widespread and distinguishable. (Fast transport allows fast plan of action)
- The SCAP pattern (development) within a plume allows to predict the spatial and temporal development, as well as the maximum extent of the organic plume.
- The SCAP pattern gives an integral signal for many parameters – stating the development of the plume from the beginning to date.
- Differential degradation must be investigated in more detail and how this reflects in the pattern.
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