Short chained alkyl phenols (SCAP)

in groundwater-

Chemical Analysis,

Adsorption Mechanism and

Field cases

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Zusammenfassung

Gegenstand dieser Arbeit ist das Vorkommen und Verhalten von kurzkettigen Alkylphenolen (SCAP) im Grundwasserabstrom der carbochemischen Industrie. An drei Felduntersuchen, welche sich bezüglich ihrer Geologie und Hydrogeologie unterscheiden, konnte gezeigt werden, daß diese Phenole selbst Jahre nach Schließung der betroffenen Standorte im Grundwasser nachweisbar sind. Da SCAP toxische und weitverbreitete Schadstoffe sind, sollte das Verhalten der individuellen Vertreter der SCAP im Grundwasser eingehender studiert werden. Dazu stellt eine präzise und richtige Analytik die Grundlage aller Felduntersuchungen dar. In diesem Zusammenhang wurden derzeit verwendete Analysenverfahren für SCAP auf ihre Anwendbarkeit und Aussagekraft für Grundwasserverunreinigungen der Carbochemischen Industrie untersucht.

Es konnte gezeigt werden, daß sich der Phenolindex gemäß DIN nicht zur selektiven Beschreibung der SCAP in Grundwasserverunreinigungen der Carbochemischen Industrie eignet. Alle SCAP reagieren mit verminderter Empfindlichkeit auf den Summenparameter. Para-Alkylphenole werden dabei gar nicht mit dem Phenolindex erfaßt. Gleichzeitig existieren in den oben genannten Schadensfällen Verbindungen wie Aniline und Heterozyklen, welche ebenfalls mit dem Phenolindex erfaßt werden, ohne dabei selbst Phenole zu sein. Daraus muß geschlußfolgert werden, daß der Summenparameter ein falsches Bild über die Verbreitung der SCAP in der Schadstoffahne zeichnet, weshalb sich auch keine Aussagen über die zukünftige Entwicklung der Kontamination ableiten lassen. Im weiteren eignet sich der Phenolindex nicht als Eingabeparameter für die Modellierung; jedoch kann der Phenolindex genutzt werden, um an einem unbekannten Standort erste Sondierungsuntersuchen durchzuführen.

Im weiteren wurden HPLC Methoden bezüglich ihrer Anwendbarkeit auf die Analytik von SCAP in komplexen Matrices getestet. Es konnte festgestellt werden, daß sich die Phenole selbst auf speziell entwickelten Säulen nicht auftrennen lassen und in komplexen Proben mit anderen Substanzen co-eluieren. Damit scheidet diese Methode für die Analytik von SCAP als Einzelsubstanzen aus.

Alle bisher beschriebenen Verfahren zur Einzelsubstanzanalytik von SCAP mit gaschromatographischen Methoden sind mit einem erheblichen Aufwand in der

Probenvorbereitung verknüpft, weshalb diese Verfahren als wenig ökonomisch für eine große Probenanzahl anzusehen sind. Umfassende Literaturstudien verweisen auf kein Verfahren, mit welchem alle 35 SCAP ohne vorrausgehende Derivatisierung direkt als Einzelsubstanzen bestimmt werden können. Daher wurde ein neues Verfahren entwickelt, mit welchem sich SCAP bei minimiertem Probenvorbereitungsaufwand als Einzelsubstanzen bestimmen lassen. Dieses Verfahren basiert auf einer geschickten Kombination neuer Entwicklungen in der Geräte- und Säulentechnik und ist als Patent angemeldet wurden. Es konnte nachgewiesen werden, daß sich underivatisierte SCAP auf einer Säule, in welcher PM-α-cyclodextrin in der metapolaren stationäre Phase gelöst vorliegt, fast vollständig auftrennen lassen. Mittels einer Solid phase microextraction aus dem Headspace der Probe (HS-SPME) konnten die Phenole wasserfrei und selektiv angereichert und auf die Säule injiziert werden. Diese Arbeitsweise gestaltet das Analysensystem verschleißarm und durch seine Automatisierbarkeit sehr ökonomisch. Es senkt dabei den manuellen Arbeitsaufwand pro Probe um ein Vielfaches gegenüber herkömmlichen Verfahren und genügt dabei den Anforderungen an Richtigkeit, Präzision und Nachweisgrenze.

Im Vorfeld zu den Felduntersuchungen wurde der Adsorptionsmechanismus der SCAP näher betrachtet. Es wurde festgestellt, daß sich die im allgemeinen leichtlöslichen SCAP anders verhalten als die üblich betrachteten Schadstoffe wie BTEX oder PAK. Auf dieser Basis kann auch das Transportverhalten jener Phenole nur ungenügend vorausgesagt werden, und eine Neubetrachtung machte sich erforderlich. Dazu wurden Batchversuche unter grundwassertypischen Verhältnissen durchgeführt, die Stufenisothermen ergaben woraus sich schließen läßt, daß es sich bei der Adsorption von SCAP an Braunkohle um eine Mehrschichtenadsorption handelt. Die Phenolschichten scheinen sich als Hemimizellen zu stabilisieren. Damit ist eine Intrapartikeldiffusion, wie sie häufig für PAK beschrieben wird, unwahrscheinlich. Langzeitversuche konnten zudem zeigen, daß die sorbierte Masse Phenol nach dem 3. Tag nicht weiter zunimmt.

Die Adsorptionskapazität kann hauptsächlich organischer Materie zugeordnet werden. Für Filterkies wurde keine Adsorption von SCAP festgestellt und auch für Karbonate (Dolomite) konnte nur wenig Adsorption gefunden werden. Generell gilt, daß die Verteilungskoeffizienten für SCAP für die oben genannten Materialien sehr viel kleiner sind, als man dies für organische Verbindungen erwarten würde. Damit sind SCAP sehr mobile Schadstoffe.

Unter den pH Bedingungen im Grundwasserleiter war keine pH-Abhängigkeit der Adsorption von SCAP an organischer Materie zu beobachten. Im Gegensatz dazu ist die Adsorption von SCAP an karbonatischen Gesteinen wie erwartet sehr wohl pH-abhängig und wird im besonderen Maße vom Ladungsneutralpunkt (ZPC) des Gesteins bestimmt. SCAP adsorbieren an karbonatischen Gesteinen im wesentlichen im pH-Fenster zwischen dem ZPC des Gesteins und der Säurekonstante des individuellen Phenols.

Ergebnisse aus 1-D Modellierungen belegen, daß die Stufenisotherme den ohnehin schon sehr geringen Retardationsfaktor weiter verringert. Im grundwasserrelevanten Konzentrationsbereich ist der mittlere Retardationsfaktor für quartäre Sedimente auf 5 bestimmt worden. Dabei gilt es jedoch zu beachteten, daß die leichter löslichen C_0 - C_1 SCAP, welche gleichzeitig durch einen ungünstigeren Verteilungskoeffizienten gegenüber dem Feststoff gekennzeichnet sind, noch über einen wesentlich geringeren Retardationsfaktor verfügen (1.2-2). Daher liegen die Retardationsfaktoren für SCAP einige Größenordungen unter den für organische Verbindungen wie PAK oder BTEX typischen Werten.

SCAP sind daher sehr mobile Schadstoffe und Adsorption als relevanter Natural Attenuation Prozeß scheidet somit für diese Stoffgruppe aus. Im gleichen Zug müssen aber auch Sanierungstechniken welche auf Adsorptionsmechanismen basieren, wie z.B. Pump & Treat, auf ihre Effizienz für SCAP hin überprüft werden. Ein erwarteter schneller Durchbruch der SCAP am Auslauf der Adsorberkolonnen könnte diese Methoden als sehr ineffektiv gestalten.

An Altlastenstandorten, welche auch SCAP enthalten, kann zusätzlich diese Schadstoffgruppe genutzt werden, um wertvolle Informationen über den Standort zu erhalten. Dazu werden in dieser Arbeit zwei Parameter vorgeschlagen. Zum einen ist dies der PCF (Phenols Cresols Fraction), mit welchem SCAP vorwiegend als Verteilungstracer genutzt werden können, zum anderen ist dies der MPR (Meta-, Paracresol Ratio), welcher sich die Eigenschaft einiger SCAP zunutze macht, unter aeroben Bedingungen selektiv abgebaut zu werden. Damit können SCAP als Sauerstofftracer eingesetzt werden. Diese Parameter werden durch eine Vielzahl von Wechselwirkungen im Grundwasserleiter erzielt, weshalb durch sie eine Art Durchschnitt der Verhältnisse im Aquifer repräsentiert wird. Im weiteren Sinne läßt sich z.B. der PCF nutzen, um Aussagen zur Art und zum Alter des Schadensherdes sowie zur Charakterisierung der Schadstoffahne zu treffen.

Abschließend ist darauf hinzuweisen, daß auch Brunnen im weiteren Abstrom auf SCAP hin zu untersuchen bzw. Brunnen im weiteren Abstrom neu anzulegen sind. Dies folgt aus der Erkenntnis, daß sich Phenole fast mit der Abstandsgeschwindigkeit und damit vergleichsweise schnell ausbreiten. In diesem Zusammenhang kann davon ausgegangen werden, daß SCAP die maximale organische Schadstoffahne beschreiben.

Schlagwörter:

Alkylphenole, SCAP, Verschwelung, Schwelteer, Felduntersuchungen, HS-SPME, PM-α-cyclodextrin, HPLC, Batchversuche, Adsorptionsmechanismus, SMART, Verteilungstracer

Abstract

The presence and behaviour of individual short chained alkylphenols (SCAP) in groundwater has been studied and is presented in this work. It could be shown on three sites, which differ in terms of their geology and hydrogeology, that SCAP are present although the operation at these sites which caused the contamination ceased long ago. SCAP are toxic and widespread contaminants which demand a detailed investigation in terms of their persistence in the environment and also in terms of their individual transport behaviour. Therefore, a sophisticated chemical analysis is required and existing analytical methods were evaluated in terms of their applicability to groundwater contaminations.

It is shown, that the *phenolindex* is not suitable for the investigation of SCAP in environmental samples. Most SCAP react with a decreased sensitivity and are underrepresented by the index. Para-alkyl SCAP are not detectable by the *phenolindex*. Simultaneously, other contaminants such as anilines and heterocyclic compounds which almost always appear together with SCAP attribute to the *phenolindex*. Therefore, it must be concluded that the sum parameter is not precise enough as an input parameter for modelling and on its basis it is rather impossible to predict the development of contamination plumes.

The separation and detection of SCAP in samples with complex matrices by HPLC methods even on specially developed columns is not recommended since some SCAP co-elute with one another or other matrix compounds. This complicates a precise analysis of SCAP and may lead to misinterpretations.

All previously reported procedures for the analysis of all individual SCAP compounds by GC methods require a substantial effort in sample preparation. In order to investigate and economically monitor those phenols in the environment the development of a cost effective, precise and robust analytical technique has been developed and evaluated on field samples. This analytical method takes advantage of the latest and commonly established developments in sample preparation and gas chromatography column technique. It could be shown that the separation of underivatised SCAP on medium polarity columns with permethyl-cyclodextrin is possible. Together with headspace SPME, for the selective, water free extraction of SCAP and their selective transfer to the GC injector, the method is economical and is operated fully automated. It is a sensitive and

selective analytical procedure which can be applied to very complex samples.

The adsorption mechanism of the highly soluble SCAP is somewhat different from commonly investigated insoluble contaminants such as PAK and BTEX. Their adsorption behaviour can not accurately be described by existing partitioning models and thus their adsorption is commonly overestimated. This requires a thorough investigation on the SCAP's adsorption mechanism which has been done by numerous batch experiments in this study. The adsorption mechanism of SCAP is that they adsorb in multi-layers onto subbituminous coal which results in a steplike isotherm. The adsorbed layers stabilise themselves by aggregating in hemimicells. SCAP do not show a great tendency to diffuse into the adsorbent and thus intraparticle sorption processes are not predominant.

The adsorption capacity is mainly assigned to natural organic matter (NOM). No adsorption was determined for coarse sand and only little adsorption was found for carbonates and dolomites. Overall, the partitioning coefficients of SCAP are very small with the consequence that they are only little retarded in aquifers. Thus, SCAP are very mobile compounds. Under groundwater relevant pH conditions SCAP adsorption onto NOM is not pH dependent. In contrast, the adsorption onto carbonate sediments is pH depended due to the nature of interaction. Generally, the adsorption capacity of carbonates increases between the point of zero charge (ZPC) of the material and the pKa of the SCAP compound.

Results from 1-D transport modelling show that the steplike isotherm effectively decreases the retardation factor. Thus, for total SCAP concentrations in the lower mg/L range the mean retardation factor of SCAP is around 5. However, the easier soluble C_0 - C_1 SCAP which have a lower distribution coefficient will have retardation factors below 5. Commonly investigated organic contaminants such as BTEX or PAH show retardation factors several orders of magnitude higher than SCAP.

SCAP were found to be very mobile compounds which implies that adsorption as a natural attenuation process does not work effectively for these compounds. Commonly applied remediation systems such as "pump and treat" and also water treatment plants which are both based on activated carbon adsorber columns do not retain SCAP for long. Their breakthrough as toxic organic contaminants happens early with the consequence that whole treatment concept for these soluble contaminants must be put into question.

The investigation of complex contaminations is always very difficult and is best done in combination of several different techniques. For sites which are contaminated by SCAP additional evidence can be gained be using the contaminants themselves as tracers. In order to do so, two parameters are suggested. The PCF (phenol cresols fraction) enables the use of SCAP as partitioning tracers and the MPR (meta- paracresol ratio) as a reactive tracer indicating the presence of oxygen in the aquifer. Thus, the SCAP distribution across contaminated sites can provide valuable information. SCAP distribution pattern are physico-chemically evolved and contain therefore some averaged information about the flow path and aquifer conditions. This in turn supports the long term prediction of the site development. SCAP are little retarded organic compounds describing the maximum extent of the organic plume and thus site investigation should therefore be carried out well beyond the source.

Keywords:

Alkylphenols, SCAP, low temperature carbonisation, coking, tar, field cases, HS-SPME, PM-α-cyclodextrin, HPLC, batch experiments, adsorption mechanism, SMART, partitioning tracer

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This work is dedicated to Elke

Es gibt Freunde
die fallen einem
so unverhofft
in den Schoß

daß man fast meint
irgendeiner hätte geahnt
daß man sie braucht

(Andrea Schwarz)

Abbreviations

AOD	Above Ordinary Datum
ASE	Accelerated Solvent Extraction
BET	Brunauer Emmett Teller
DAD	Diode Array Detector
DCM	Dichloromethane
DMP	Dimethylphenol(s)
EC50	Effective Concentration 50%
ED	Electrochemical Detector
EDC	Endocrine Disrupter Compound
EGA	Evolved Gas Analysis
EPA	Environment Protection Agency
FIAS	Flow Injection Analytical System
GCMS	Gas Chromatography Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IR	Infrared
LLE	Liquid-Liquid Extraction
LTC	Low Temperature Carbonisation
MAE	Microwave Assisted Extraction
MNA	Monitored Natural Attenuation
NOM	Natural Organic Matter
OW	Observation Well
PA-fibre	Polyacrylate fibre
SCAP	Short Chained Alkylphenols
SEI	Surface Excess Isotherm
SFE	Supercritical Fluid Extraction
SIM	Selected Ion Monitoring
SOM	Solid Organic Matter
SPE	Solid-Phase Extraction
SPME	Solid-Phase Micro Extraction
TMP	Trimethylphenol(s)
URS	Ultraviolet Ratio Spectrophotometric System
UV-VIS	Ultraviolet-Visuable
XRD	X-Ray Diffractometry
ZPC	Zero Point of Charge

Preface

This thesis is to be regarded as a part of an ongoing study on the behaviour of SCAP in the subsurface. It represents the final work of my Ph.D. study within the Hydrogeological Group at the Department of Geological Sciences, Faculty of Chemistry and Earth Sciences, Friedrich Schiller University of Jena and within the Department of Hydrogeology of the Environmental Research Centre Leipzig-Halle Ltd. in Halle. It serves as documentation of my own work between autumn 1999 and summer 2002.

Alkylphenols came forcibly to my attention while I was employed as a research assistant on the aquifer vulnerability project M25 at the University College in London. I had determined SCAP in low concentrations in well water which supplied a brewery at this time. Investigations showed that the well was influenced by a discontinued gas works site close by. The analysed presence of SCAP at this well even 70 years after gas production had ceased stood in clear contradiction to the general believes on this group of contaminants to be easily degradable.

When I started my Ph.D. studies in Jena in July 1999 I was given 6 month to shape a project which is of importance to the federal state of Thüringen (Thuringia). I soon learned about the extensive contamination which the closed down tar processing plant Rositz had left behind and where SCAP might be key contaminants. I remembered the findings from London and decided to take up research on this field as my supervisor agreed to this idea. An extensive literature review revealed little on the environmental behaviour of SCAP as they are little investigated to date.

My research started with the intensive assessment of chemical analytical methods as applied to SCAP. This assessment led to the development of an easier analytical method for the determination of SCAP as individual compounds. Unfortunately, the institute in Jena did not have access to a GC-MS instrument and such an instrument could not be made accessible in Jena. HPLC methods were not satisfactory in their separation efficiency for real samples or to put it in other words "*standards looked great but real samples didn't*" which is not a good base to start research on. During my undergraduate studies I have often worked in the Department of Hydrogeology, UfZ (Environmental Research Centre Leipzig-Halle Ltd.). Those connections now became very helpful as I was given access to a fully equipped analytical organic chemistry laboratory. Furthermore,

there was ongoing research on the deep injection of phenol contaminated low temperature carbonisation water at the UfZ and thus access to real samples was provided which did not only support the development of the analytical method but also the development of ideas on their behaviour in the subsurface. In total, about 1500 analyses have been carried out during this study. This simultaneously meant commuting between Jena and Halle for the time of this study between 2000 and 2002 and the stories on travelling with DEUTSCHE BAHN AG would already fill a book.

The research has been accomplished by laboratory batch experiments done in Jena to investigate the adsorption mechanism of SCAP. All experiments have carefully be thought out and set up in order to achieve an optimum an information and cancel out artefacts. This series of batch experiments comprises more than 1000 batch samples, which needed to be prepared, stored, analysed and evaluated.

During my studies on alkylphenols I learnt the meaning of the words: “Eine vorgefertigte Meinung ist schwerer zu zertrümmern als ein Atom” - ”It is more difficult to destroy a preconceived idea than an atom.” (A. Einstein). It seems often more complicated to bring up new ideas on something old than to work on something completely new.

The important thing

in science is

not so much

to obtain new facts

as

to discover new ways

of thinking about them.

Sir William Bragg

1 General introduction

In the mid 1970s the coking plant “Dortmund Dorstfeld” was closed down. Early in the 1980s, the city council sold land on these premises cheaply to socially underprivileged families for founding a housing estate. In the mid 1980s, people became more frequently sick than other people in this area. Investigations started when brownish waters finally seeped into their cellars from below. The results of this investigation yielded a high short chained alkylphenol (SCAP) concentration in the water and soil. Medical experts estimated the cancer risk for people who had lived on these premises a 1000 times higher than average. Nowadays, the housing estate is being pulled down and the city council had to pay a substantial compensation to these families (WEIDENBACH & HEMSCHEMEIER (2001)).

1.1 Current understanding on SCAP in the environment

Early research on SCAP in groundwater was conducted by EHRLICH et al. (1982). They described the impact of contaminants from a coal-tar distillation plant on the groundwater quality. Phenols were analysed by a sum parameter but not as individual SCAP. Their conclusion from this phenomenological approach is that phenols are easily degradable compounds, even under methanogenic conditions. Other approaches deal with contamination plumes from coal tar plants or creosote spills (e.g. ENGWALL *et al.* (1999), GODSY *et al.* (1992A), GODSY *et al.* (1992B), GOERLITZ *et al.* (1985) , GUERIN (1999)) but SCAP were again not reported as individual compounds.

More recently, studies on plumes from old town gas and coking plants started to focus on individual SCAP compounds (LERNER *et al.* (2000)) which however included only selected SCAP.

General regulations concerning threshold values for SCAP in water or waste materials have not yet been established. This may be due to the lack of appropriate chemical analytical methods. No fast, easily applicable and cost effective analytical method was available for the analysis of SCAP as individual compounds. So far, only two regulations for phenols have been established. These are threshold values for priority phenols according to EPA (EPA (1996) and a sum parameter threshold value. The list of priority phenols includes only 4 SCAP which are the 3 cresols and 2.4-dimethylphenol. The other even more toxic SCAP (compare toxicity data in Tab. 4) are not accounted for in the EPA directive. The sum parameter however accounts for total phenols and most directives world wide contain such threshold values. Those sum parameter threshold values can not account for the vast difference in the SCAP’s toxicity. In the worst case the degree of toxicity from the individual SCAP components are unrecognised.

In Germany, the drinking water act from 1990 (TRINKWV (1990)) includes a threshold value for the sum parameter of 50 µg/L. In 2003 this directive will be replaced by a new version with a threshold value for phenols no longer included. The phenol sum parameter threshold values for groundwater, soils and waste are regulated in Germany by the soil protection act (BODSCHG (1995)), which only occasionally contains such values.

In Europe, the "COMMISSION OF THE EUROPEAN COMMUNITIES" published a list of priority substances in the field of water policy (EU (2000)). So far, this list only contains C8 and C9 alkylphenols and pentachlorophenol. No threshold values for individual SCAP nor for the phenol sum parameter are given there.

1.2 Motivation and objectives

The environmental behaviour of individual SCAP compounds in groundwater has not been studied in great detail. This is most likely due to the lack of an easy applicable chemical analytical method for their determination in heavily contaminated samples. Their overall presence or absence today is commonly described by insensitive sum parameters such as "*Phenolindex*". However, as will be pointed out in more detail in chapter 2.3, SCAP are toxic and widespread contaminants, which demand better investigation in terms of their persistence in the environment and also in terms of their individual transport behaviour. The following questions briefly summarise the motivation and objectives of this thesis.

The problems:

- Which SCAP exist in groundwater in the vicinity of various coal processing plants? In what relative proportion to each other do they occur?
- How do sum parameters describe the SCAP plume on such sites?
- How can individual SCAP be economically determined in complex matrices?
- How can the transport behaviour of SCAP in the subsurface be described?
- Which factors may influence their transport behaviour (aquifer material, pH)?
- How does the shape of their respective isotherms effect their transport behaviour?
- What can be concluded from their investigated transport behaviour?

The procedures:

- Analysis of 23 SCAP individually by the “phenolindex” to describe their quantitative and qualitative contribution to the sum parameter
- Analysis of synthetic test mixtures and field samples by the “phenolindex” to investigate the information contained in the sum parameter for phenolic contaminations in the subsurface
- Comparison of phenolindex with individual SCAP concentrations
- Development of an easy applicable, fast and robust chemical analytical method for the analysis of SCAP as individual compounds in complex matrices
- Sampling and analysis of groundwater in 3 aquifer types at various coal processing plants at 5 sites
- Sampling and analysis of drilling cores at 2 sites
- Investigation of the SCAP distribution pattern on these sites
- Investigation of the adsorption mechanism by several controlled batch experiments on different materials

The flow diagram in Figure 1 shows the different aspects of this work and how they connect to give the whole picture.

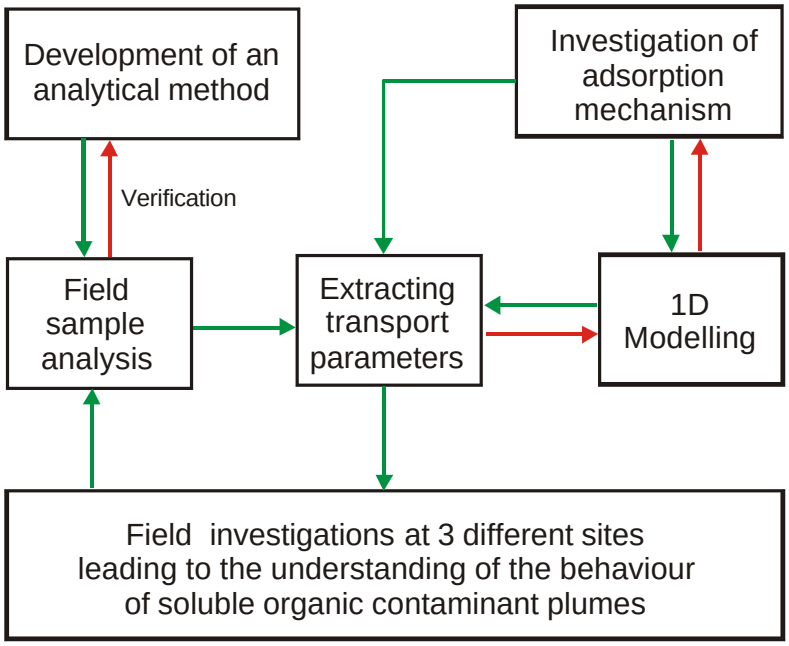


Figure 1: Flow diagram of this study and how the different parts connect together

2 Short chained alkylphenols (SCAP)

2.1 Phenols - a diverse group of chemical compounds

Phenols are hydrocarbon derivatives containing at least one hydroxyl group [OH] group bound to an aromatic ring. This general or rather ambiguous definition allows to summarise many chemical compounds with very different properties into one class of components. Only some of these are toxic. Figure 2 gives an idea on a common classification together with main aspects of their diverse toxicological and physico-chemical properties. Further details on properties and toxicity of the classified phenolic subgroups from Figure 2 can be found in Tab. 1.

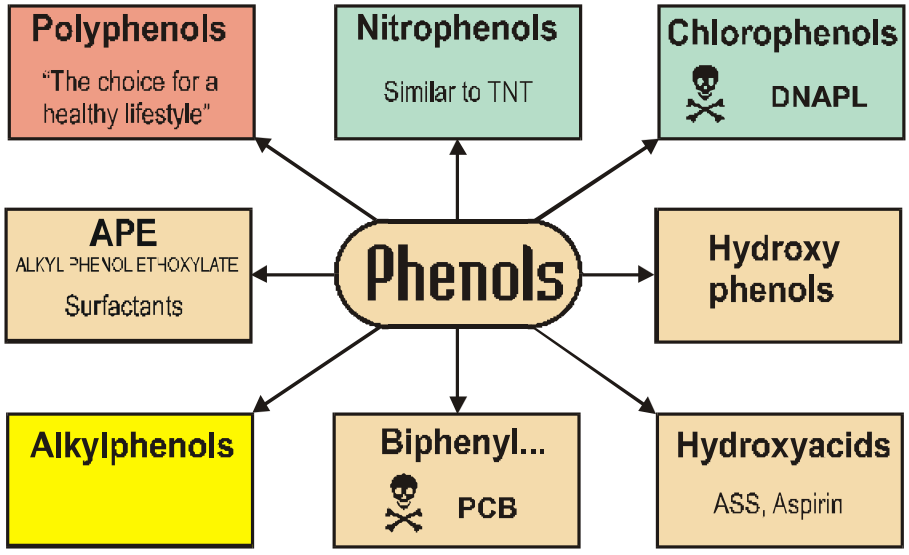


Figure 2: Common classification of phenolic compounds

Tab. 1: Properties, toxicity and usage of the phenolic subgroups

Subgroup	Properties	Toxicity	Usage/source
Chlorophenols	Soluble, DNAPL, persistant	very high	Pesticide
Biphenyl	Insoluble, persistant	very high	Pesticide, hydraulic fluid
Nitrophenols	Soluble, persistant	High	Explosives
APE	Soluble, Surfactant	Low	Surfactant
Hydroxyphenols	Highly soluble, labile	Low	Developers
Hydroxyacids	Highly soluble	Low-medium	Pharmaceuticals
Polyphenols	Nonsoluble	No	Health products
Alkylphenols	Very inhomogeneous group, see next chapter		

Unlike the toxic chloro- and nitrophenols, which are already listed as priority pollutants, alkylphenols were not investigated in great detail. This work therefore focuses on a subgroup of the alkylphenols, the short chained alkylphenols.

2.2 Alkylphenols- from Endocrine Disrupters to SCAP

The subgroup alkylphenols includes only phenols where hydrogen atoms from the benzene ring are substituted by alkyl groups of various chain length. The number of carbon atoms outside the ring is often given in the form C_X, where C stands for carbon and x for the number of atoms outside the ring. Figure 3 shows a suitable classification for alkylphenols, which accounts for their different solubility, toxicity and usage.

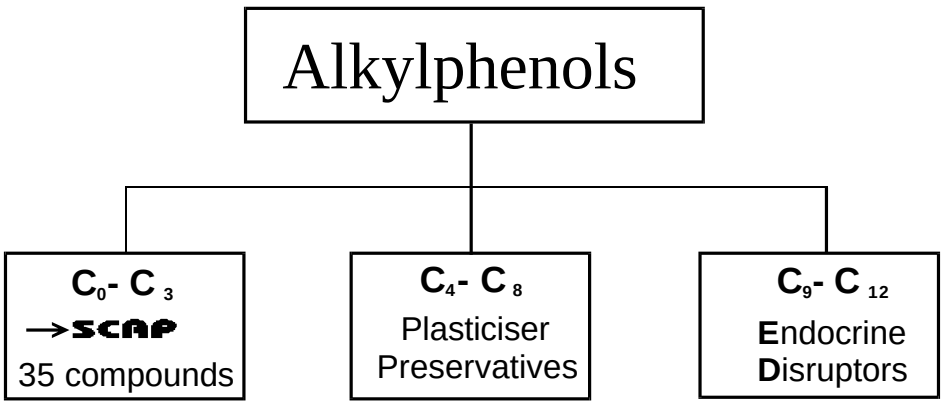


Figure 3: Suggested classification of environmentally relevant alkylphenols

To clearly separate this subgroup from other alkylphenols the abbreviation SCAP is introduced in this study. Short chained alkylphenols are comprised by the following 8 groups with their respective isomers (Figure 4). In total, SCAP include 34 short chained alkylphenols (C_1-C_3) and phenol (C_0):

i.) Phenol (C_0)
ii.) Cresols (C_1) with 3 isomers
iii.) Dimethylphenols (C_2) with 6 isomers
iv.) Ethylphenols (C_2), with 3 isomers
v.) Trimethylphenols (C_3) with 6 isomers
vi.) Ethyl methylphenols (C_3) with 10 isomers
vii.) n-Propylphenols (C_3) with 3 isomers
viii.) i-Propylphenols (C_3) with 3 isomers

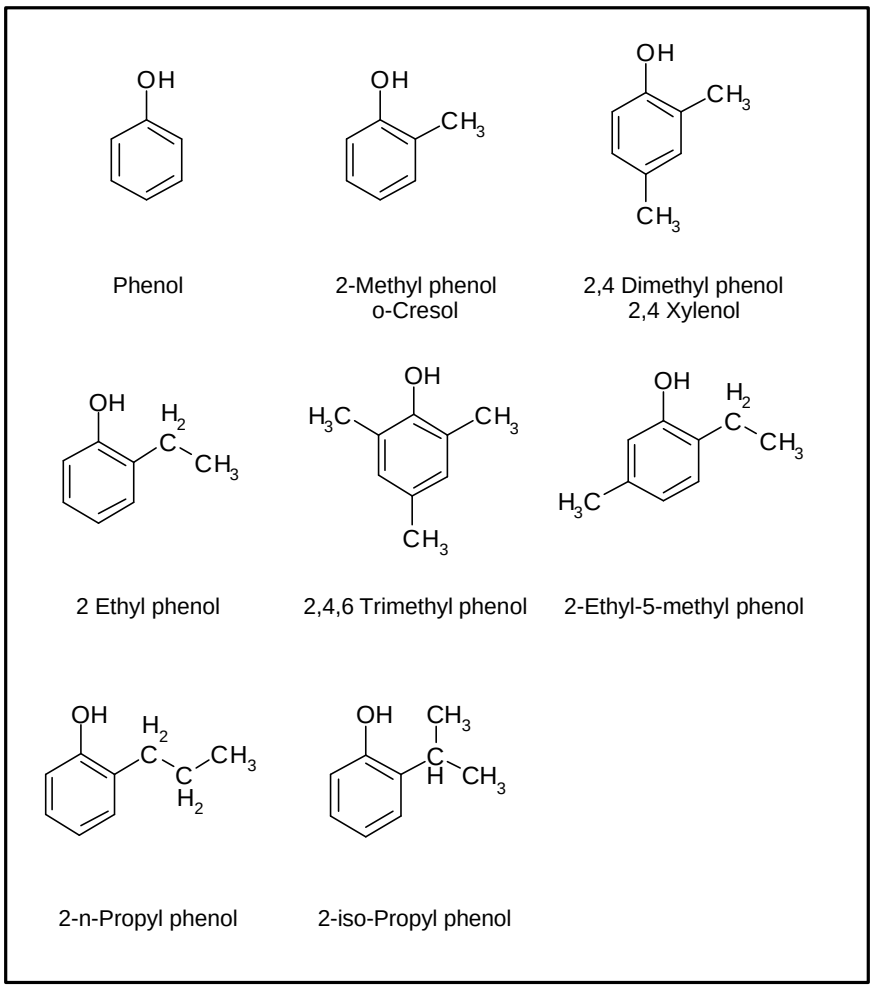


Figure 4: Chemical formula of an example from each of the 8 SCAP subgroups

2.3 Main Properties of SCAP

Concise data sets are only reported for some isomers. In fact, no data are available for approximately 30% of all 35 compounds. Their precise environmental behaviour therefore remains speculative.

The application of quantitative structure-activity relationships (QSAR) may be helpful for the estimation of missing data. A WINDOWS based program called EPI-suite is a public domain program provided by the US-EPA. It contains several environmentally relevant subprograms using QSAR. Two subprograms PCKOCWIN and HENRYWIN were applied to calculate the octanol/water partition coefficient (K_{OW}), the soil adsorption coefficient (K_{OC}) and the dimensionless Henry coefficient (H) for two temperatures (groundwater: 15°C and temperature of headspace analysis: 50°C)

Soil adsorption coefficient and octanol/water partition coefficient: The soil adsorption coefficient subprogram (PCKOCWIN) estimates the soil adsorption coefficient (K_{OC}) of organic compounds. K_{OC} can be defined as "the ratio of the amount of a compound

adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the compound in solution at equilibrium". K_{OC} provides an indication of the extent to which a compound partitions between solid and solution phases in soil, or between water and sediment in aquatic ecosystems. Traditional estimation methods rely upon the octanol/water partition coefficient (K_{OW}) or related parameters. Recently the first-order molecular connectivity index (1-MCI) has been used successfully to predict K_{OC} values for hydrophobic organic compounds (MEYLAN *et al.* (1992)). PCKOCWIN uses 1-MCI and a series of group contribution factors to predict K_{OC}. The group contribution method outperforms traditional estimation methods based on octanol/water partition coefficients and water solubility (BAKER *et al.* (2000)). The developed new estimation method (MCI) and series of statistically derived fragment contribution factors for polar compounds in PCKOCWIN extend the model to polar compounds. Results confirm that the model covers a wider range of chemical structures than models based on octanol-water partition coefficients (K_{OW}) or water solubility do (BAKER *et al.* (2000)).

Henry coefficient:The program (HENRYWIN) estimates the Henry coefficient (H) at 25°C using the methodology originally described by HINE & MOOKERJEE (1975). The original methodology has been updated and expanded at Syracuse Research Corporation (MEYLAN & HOWARD (1991)). HENRYWIN allows the estimation of H for an environmentally relevant temperature range (0°C to 50°C) and requires only a chemical structure to make these predictions. The Henry coefficient is estimated by two separate methods that yield two separate estimates. The first method is the bond contribution method and the second is the group contribution method. The bond contribution method is able to estimate many more types of structures; however, the group method estimate is usually preferred (but not always) when all fragment values are available. The data provided in Tab. 2 are calculated applying the bond contribution method. The Henry coefficient in Tab. 2 are provided for groundwater relevant conditions and for the temperature applied in chemical analytical method (HS-SPME) later described in this study.

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

Tab. 2: QSAR derived properties of SCAP, chemical abstracts number (CAS), dimensionless Henry coefficients, comparison of calculated and experimental partitioning coefficients

SCAP		CAS	Henry coefficient dimensionless		log K_{OW} calculated	log K_{OW} experimental	log K_{OC} calculated
			50°C	15°C			
Phenol	C_6H_6O	108952	0.55 e10^{-4}	0.138 e10^{-4}	1.51	1.46	1.25
o-Cresol	C_7H_8O	95487	2.82 e10^{-4}	0.224 e10^{-4}	2.06	1.95	1.74
m-Cresol		108394	1.87 e10^{-4}	0.164 e10^{-4}	2.06	1.96	1.75
p-Cresol		106445	2.80 e10^{-4}	0.172 e10^{-4}	2.06	1.94	1.73
2.3-DMP	$C_8H_{10}O$	526750	1.71 e10^{-4}	0.138 e10^{-4}	2.61	2.48	2.27
2.4-DMP		105679	2.21 e10^{-4}	0.178 e10^{-4}	2.61	2.3	2.09
2.5-DMP		95874	2.60 e10^{-4}	0.210 e10^{-4}	2.61	2.33	2.12
2.6-DMP		576261	15.4 e10^{-4}	0.825 e10^{-4}	2.61	2.36	2.15
3.4-DMP		95658	0.96 e10^{-4}	0.077 e10^{-4}	2.61	2.23	2.02
3.5-DMP		108689	1.42 e10^{-4}	0.115 e10^{-4}	2.61	2.35	2.14
2-EP	$C_8H_{10}O$	90006	10.7 e10^{-4}	0.863 e10^{-4}	2.55	2.47	2.26
3-EP		620177	1.38 e10^{-4}	0.120 e10^{-4}	2.55	2.4	2.19
4-EP		123079	1.70 e10^{-4}	0.148 e10^{-4}	2.55	2.58	2.37
2.3.5-TMP	$C_9H_{12}O$	697825	1.53 e10^{-4}	0.150 e10^{-4}	3.15		
2.3.6-TMP		2416946	8.02 e10^{-4}	0.782 e10^{-4}	3.15	2.67	2.46
2.4.5-TMP		496786	1.53 e10^{-4}	0.150 e10^{-4}	3.15		
2.4.6-TMP		527606	5.29 e10^{-4}	0.516 e10^{-4}	3.15	2.73	2.52
3.4.5-TMP		527548	1.53 e10^{-4}	0.150 e10^{-4}	3.15		
2-n-PP	$C_9H_{12}O$	644359	2.22 e10^{-4}	0.216 e10^{-4}	3.04	2.93	2.72
3-n-PP		621272			3.04		
4-n-PP		645567			3.04	3.2	2.99
2-i-PP	$C_9H_{12}O$	88697	2.22e10^{-4}	0.216 e10^{-4}	2.97	2.88	2.67
3-i-PP		618451			2.97		
4-i-PP		99898			2.97	2.9	2.69

Aqueous solubility: SCAP are water soluble compounds with solubilities considerably higher than other common organic contaminants such as BTEX or PAK. This effect is caused by their ability to participate in hydrogen bridging bond systems. Since hydrogen is intensely attracted to small, electron-rich atoms such as oxygen, 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 & LARTER (1997) describe this solubility influence of substituents with the help of oil-brine partitioning data. Solubility data obtained by VARHANICKOVA *et al.* (1995) show the opposite (Tab. 3). Their solubility varies between the individual compounds and decreases from C_0 to C_2 by approximately two orders of magnitude.

Tab. 3: Solubilities of individual SCAP compounds at 25°C[1]

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

Toxicity: Since SCAP toxicity data for humans are not available, analogies must be applied from data gained in microbial test 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 result from different metabolic pathways, increased lipophilic character and an increased residence time in the organism. It may also be entirely different for humans, if not much lower (EISENBRAND & METZLER (1994)). SCAP are toxic to 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 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. The available data are summarised in Tab. 4.

Tab. 4: Available toxicity data of SCAP[2]

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		

[1] Data from VARHANICKOVA *et al.* (1995)
[2] Toxkit microbiotests data from KAHRU *et al.* (1999)

2.4 Sources and Environmental Relevance of SCAP

SCAP are generally produced when complex organic matter (mainly plants) is thermally treated under anaerobic conditions. They are naturally produced during the formation of crude oil (TAYLOR *et al.* (1997), BENNETT *et al.* (1996)). Therefore, crude oil production waters will contain substantial amounts of the highly soluble SCAP. Coal does not contain SCAP naturally. However, SCAP are generated by pyrolytic breakdown of lignite during the technical processes used to convert coal into town gas and raw materials for the chemical industry as a crude oil substitute. Thus SCAP are found in smouldering condensation waters, tar and tar oil as well as in other by-products from these processes.

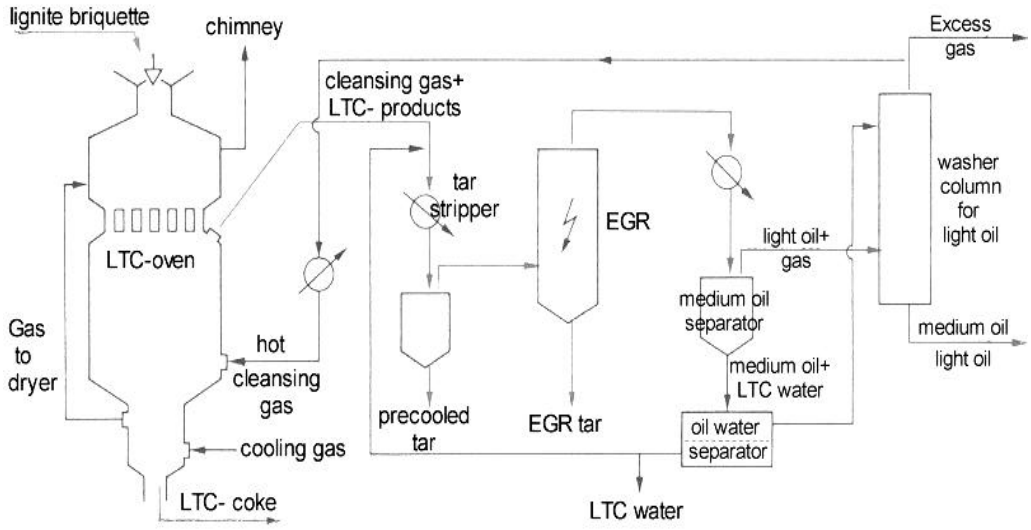


Figure 5: Sketch of a LTC plant with Lurgi Cleansing Gas Technology (ABC CHEMIE (1987))

Figure 5 displays the flow diagram of a typical Lurgi low temperature carbonisation (LTC) plant. The Lurgi Cleansing Gas Technology was one of the most frequently applied low temperature carbonisation techniques across Europe (LISSNER & THAU (1953)). Until the 1960s, it provided town gas, important carbo chemicals for a rapidly developing chemical industry and coke for the metallurgic industry. Beside the Lurgi-process, the Rolle-process was used as an alternative method in central Germany, i.e. in Groitzschen (KIESL (1997)). However, large quantities of SCAP rich LTC water remain as a hazardous by-product. This water was mainly dumped close by in closed open cast mines. A well known example is the phenol lake Schwelvollert (WIEßNER *et al.* (1993)).

Only when in 1970 the Phenol-Solvan-Technology became popular the SCAP concentration in the LTC water was reduced (HUTH (1972), PLÖTTNER (1997)). Today, a determining petrol chemistry/industry and a reduced lignite mining lead to the almost complete disappearance of the carbonisation technique in Germany.

Coal is a natural product and like any other natural product subject to a high variation in its composition. Since the major source for phenols is lignite- its proportion in coal largely determines the phenol formation during carbonisation. The technological processes determine further SCAP output and composition. A historical regional variation and process dependency is given in Tab. 5.

Tab. 5: Creosote in various lignite tars from mining areas in central Europe [3] [4]

Mining Area	Process/ Product Type	Creosote (vol %)
Anhalt	Kosag-Geißen/ LTC- Tar	11.2
Borna	Lurgi-CGC/ EGR Tar	9.2 wt %
Helmstedt	Lurgi-CGC/ EGR Tar	16
Lower Lusatia	Lurgi-CGC (1955)/Circulation Tar	20.2
Lower Lusatia	Lurgi-CGC (1958)/ EGR Tar	21.1
Rhine area	Shaft Generator/ Generator Tar	22
Thuringia	CBG/ Generator Tar	10
East Elbian	Koppers/ Generator Tar	15.7
Saxonia	OPG/ Generator Tar	9
Bohemia	OPG/ Generator Tar	18

As shown in Tab. 5, the creosote proportion in lignite tars varies from 9 to 22 vol%. Creosote stands for a whole class of compounds with acidic properties. In other words, everything in the tar, that is soluble in aqueous bases. It consists mainly of longer chained organic acids (C7-C12) and SCAP. Creosote has extensively been used as a wood preservative in some parts of Europe such as Scandinavia and also in the United States. To enhance its wood preserving properties some companies additionally added pentachlorophenol which dramatically increased its overall toxicity. SCAP only represent a portion of the compounds in tar creosote (Tab. 7). The LTC tar from East Elbian lignite coal typically contains 10-12 vol% creosote, but only 2.65 vol% SCAP. In other words, the creosote fraction is made up of around 25% SCAP. This is not very surprising since SCAP have boiling points in the 100-160°C region and tar is the remaining distillation fraction with boiling points of usually more than 200°C. This also explains the approximately 10 times higher SCAP concentration in the earlier distillation fractions such as medium and

[3] in GUNDERMANN (1964)

[4] CGC: cleansing gas carbonisation, LTC: low temperature carbonisation, EGR: electro gas purification, CBG: cabonisation generator OPG: oxygen pressure gassification, HTC: high temperature carbonisation

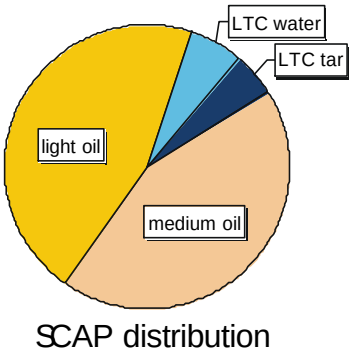
light oil. At several carbonisation sites tar and oils were only by-products and have therefore not been separated. In such cases, the SCAP concentration in those tars is higher. Furthermore, the variation of the creosote proportion in the light oil is subject to a higher variability (Tab. 6). Its content varies from 3.8% to 25.2%.

Tab. 6: Creosote variation in light oil fraction [3 4]

Mining Area	Process	Creosote wt %
Anhalt	Kosag-Geißen	3.8
Saxonia I	Lurgi-CGC	5.0
Saxonia II	Lurgi-CGC	10.0
East Elbian	HTC, chamber oven	25.2

Tab. 7: SCAP proportion in 5 carbonisation fractions [3 5 6]

Product Type	C_0-C_1 Vol%	C_2 Vol%	C_3 Vol%	SCAP Vol%
LTC Tar [2]	0.50	0.96	1.19	2.65
Medium Oil [2]	12.0	7.0	3.8	22.80
Light Oil [2]	13.7	6.1	3.8	23.60
LTC waters [4] (Hirschfelde)				2.8-3.2
Crude Oil [5] (North Sea)	0.025	0.017	0.010	0.052

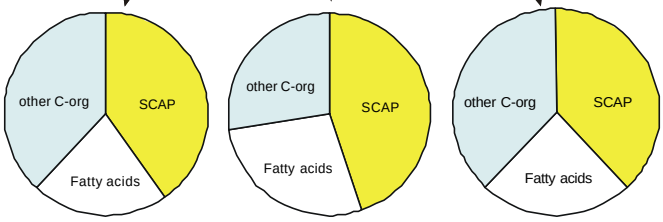


The proportion of SCAP in the LTC product fractions are shown in Tab. 7. The LTC waters contain beside SCAP larger quantities of ammonia, methyl alcohol, acetic acid and hydrogen sulphide (HUTH (1972), GUNDERMANN (1964), v. ALBERTI (1983)). The composition of lignite together with their SCAP proportion in relation to TOC are displayed in Tab. 8. To summarise, the coal processing industry contributes the largest proportion of anthropogenically produced SCAP to the environment.

[5] in LISSNER & THAU (1953)
[6] in BENNETT *et al.* (1996)

Tab. 8: Three examples for the composition of LTC waters

component in g/L	Böhlen	Hirschfelde	Espenhain
H_2CO_3	4.0-5.6	0.5-2.0	3.7-4.6
H_2S	0.1-0.2	0.05-0.1	1.2-2.1
$NH_{3\,total}$	5.5-6.7	2.1-5.2	6.4-7.6
S_{total}	0.7-1.0	0.7-1.2	2.2-2.6
SCAP	12.8-15.2	28.0-32.0	19.3-21.2
Fatty acids	6.8-8.4	17.0-20.0	12.4-13.0
C_{org}	13.0-13.5	18.5	20.3
pH	8.7	5.0-7.5	8.0-8.4



Organic carbon composition (TOC)

In summary, SCAP were widespread contaminants across Europe originating from various sources. Most widespread source are manufacturing gas plants, since many towns had their own plant. The industry with numerous coking plants, smouldering plants, tar lakes, creosote spills and crude oil production waters represent the second most important SCAP source. Furthermore SCAP are used as petrol stabilisers in Europe (SCHMIDT *et al.* (2001)). It is estimated that at least 3000 SCAP contaminated sites exist across Europe. Under these aspects the question arises, why not all SCAP are not considered as “priority pollutants”. Only phenol, cresols and 2.4-dimethylphenol are listed as “priority pollutants” and consequently their environmental impact has been investigated.

2.5 Degradability of SCAP

All SCAP can potentially be degraded under aerobic conditions (MÜLLER *et al.* (1991), NIELSEN & CHRISTENSEN (1994)). Degradation of phenol, o-cresol, m-cresol, p-cresol, 2.4-dimethylphenol and 3.4-dimethylphenol has been observed under anoxic (nitrate and/or iron reducing) conditions in laboratory experiments (LOVLEY & LONERGAN (1990), FLYVBJERG *et al.* (1993), NIELSEN *et al.* (1995)) whereas 2.3-, 2.5-, 2.6- and 3.5-dimethylphenol were persistent under nitrate reducing conditions (FLYVBJERG *et al.* (1993)). Phenol was degraded in the field under anoxic conditions (NO_3^- /Fe reducing) in a leachate plume after a long lag-phase, but o-cresol was shown to be persistent (NIELSEN *et al.* (1995)). The results from lab microcosm studies (M), batch reactor experiment (B) and from field investigations

concerning the microbial degradability of SCAP are summarised in Tab. 9.

Tab. 9: Degradability of SCAP under the various redox conditions

Name	Aerobic		Nitrogen reduction		Fe/Mn reduction		Sulphate reduction		CH4 Genesis	
	pos.	neg.	pos.	neg.	pos.	neg.	pos.	neg.	pos.	neg.
Phenol	M1 M3 M5 M11 M15 M16 B2 B3		M1 M2 M5 M9 M11 M14 B2 M17		M7 M9 M11 M17		M1 M5 M8		M1 M4 M5 M8 M14	
	F1 F2/3		F4 F5		F2/3 F5		F2/3			
o-Cresol	M3 M11 M15 M16		M9 M11 M14 M17	M2 B1	M9 M11 M17			B1	M14	B1
	F1			F5		F5				
m-Cresol	M3 M15 B2 M16		M3 M14 B2 M17 M18		M17		M6 M18		M10 M14	M18
p-Cresol	M3 M11 M15 M16		M2, M3 M9 M11 M14 M17		M7 M9 M11 M17		M8		M8 M14	
2,3 DMP	M15			M13 M17		M13		M13		M12 M13
2,4 DMP	M3 M15		M17	M13	M17	M13		M13		M12 M13
2,5 DMP	M3 M11 M15		M9 M11	M13 M17	M9 M11	M13 M17		M13		M12 M13
2,6 DMP	M3 M15			M9 M13 B1 M17		M9 M13		M9 M13 B1		M12 M13 B1
	F1 F2/3				F2/3		F2/3			
3,4 DMP	M11 M15		M9 M11 M17	M13	M9 M11 M17	M13		M13		M12 M13
3,5 DMP	M11 M15		M9 M11	M13 M17	M9 M11	M13		M13		M12 M13
	F1									
2-EP				M13 B1		M13		M13 B1		M12 M13 B1
¾-EP				M13		M13		M13		M12 M13
TMP	No data avaliable on these SCAP									
PP										

M1: Pickup et al. (2001), M2: Spence et al. (2001), M3: Harrison et al. (2001), M4: Kobayashi et al. (1989), M5: van Schie & Young (2000), M6: Müller et al. (1999), M7: Lovley et al. (1989), M8: Wang & Barlaz (1998), M9: Broholm, M. et al. (2000), M10: Londry & Fedorak (1993), M11: Broholm & Arvin (2000), M12: Grbic-Galic (1990), M13: Thomas & Lester (1993), M14: O'Connor & Young (1996), M15: Müller et al. (1991), M16: Nielsen & Christensen (1994), M17: Flyvbjerg et al. (1993), M18: Ramanand & Suflita (1991), B1: Puig-Grajales et al. (2000), B2: Fang & Zhou (1999), B3: Buitron et al. (1993), F1: Broholm, K. et al. (2000), F2: King & Barker (1999), F3: King et al. (1999), F4: Davison & Lerner (1998), F5: Nielsen et al. (1995),

M : laboratory microscosm study, B: batch experiments, F: field investigations

3 Introduction to analytical methods as applied to SCAP

This chapter summarises the most common chemical analytical techniques as applied to phenols. Information was taken from periodicals, from textbooks and from the internet. The internet sources are cited in footnotes at the respective positions. The textbooks used are as follows: BUCH DER UMWELTANALYTIK (1-4) (1998), MACALADY (1998), PAWLISZYN (1997), HEIN & KUNZE (1995), DOERFFEL *et al.* (1994), SMITH (1993), SKOOG & LEARY (1992), WAGNER & YOGIS (1992). The first section explains how to determine the extent of phenolic contaminations by means of sum parameters. It introduces the reader to various commonly applied parameters, especially to the German *Phenolindex*. A concise description of this parameter, including the step by step reaction equations, is provided. The next section introduces the sample preparation methods commonly applied to phenol analysis from aqueous and solid environmental samples. The last section describes the here applied chemical analytical techniques based on chromatographic separations.

3.1 Sum Parameters for Phenolic Compounds

Sum parameters have first been developed for the easy and cost effective monitoring of hazardous waste waters from industrial plants. Meanwhile, several sum parameters like AOX, DOC or IC are well established. However, sum parameters are by definition not capable of differentiating between individual compounds.

Early sum parameter developments for phenols were mainly based on the evaluation of chlorophenols and/or nitrophenols in industrial effluents. Currently, several standardised sum parameters exist, such as:

- ISO-6439:1990 (Canada, Poland, Czech Republic, Republic of Slovakia, Republic of Lithuania, Malta, Russia)
- EPA 9065, EPA 402.20 (Canada, USA)
- DIN 38409- H16, commonly referred to as *phenolindex* (Germany, Austria, Switzerland)
- BS 6068-2.12:1990 (UK, Republic of Ireland, British Common Wealth)
- APHA Standard Methods 19th ed. P5-33 method 5530D (Europe)
- ASTMD 1783-91 (application area unknown)

The working procedures for the respective standardised sum parameters do not differ much from each other and are based on the formation of a dye. Modifications are for example based on the change of the oxidising agent form potassium peroxidisulphate to potassium ferricyanide (HASSAN *et al.* (1987), Majewskaja (1941)).

Most samples require a special treatment, such as the removal of sulphite or a preliminary

distillation to remove interferences. Phenols belong to the group of steam volatile organic compounds which enables the distillation of an acidified sample to yield the phenolic distillate. Acidification increases the yield of phenols in the distillate and discriminates basic steam volatile compounds such as aniline which would also distil over. However, it is questionable whether this discrimination works quantitatively.

The colour reaction between phenol and 4-AAP was first investigated in greater detail by EMERSON (1943) for its applicability to various phenols. He reports that many substituted phenol dyes do not have the same molar specific absorbance as phenol. How well the priority phenols (phenols from EPA, METHOD 604 (1984)) can be detected by the 4-AAP method is reported by e.g. NEUFELD & PALADINE (1985). The reasons for the different detectabilities of the various phenolic compounds by the 4-AAP method is explained by BARTON *et al.* (1987). They report the various structures of the pyrazolones formed by the oxidative coupling of phenols with 4-AAP in aqueous solution. Because phenolic-type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as calibration standard. This is why phenol has been selected as a standard and any colour produced by the reaction of other phenolic compounds is reported as phenol.

The German standard method - Phenolindex The German standard DIN 38409/H16 is very similar to the American method: EPA, METHOD 9065 (1986). It is commonly referred to as *phenolindex* and divided into 3 sections:

- H16/1: Determination of the *phenolindex* after dye extraction
- H16/2: Determination of the *phenolindex* after distillation and dye extraction
- H16/3: Determination of the *phenolindex* after distillation

After the dye has formed (30-60 minutes) it is extracted into chloroform and the extract filled into a 25ml vial through anhydrous sodium sulphate, which removes water traces from the organic phase. Immediately after extraction its absorption is determined at 460nm. Hereby it needs to be assured that the absorbance is determined relative to a blank sample. This is especially important, if the reactants (4-AAP, $K_2S_2O_8$) are not freshly prepared. Once prepared, reactant solutions easily oxidise and turn brownish. This lets them adsorb at the determination wavelength of 460nm leading to an insufficiently high blank value.

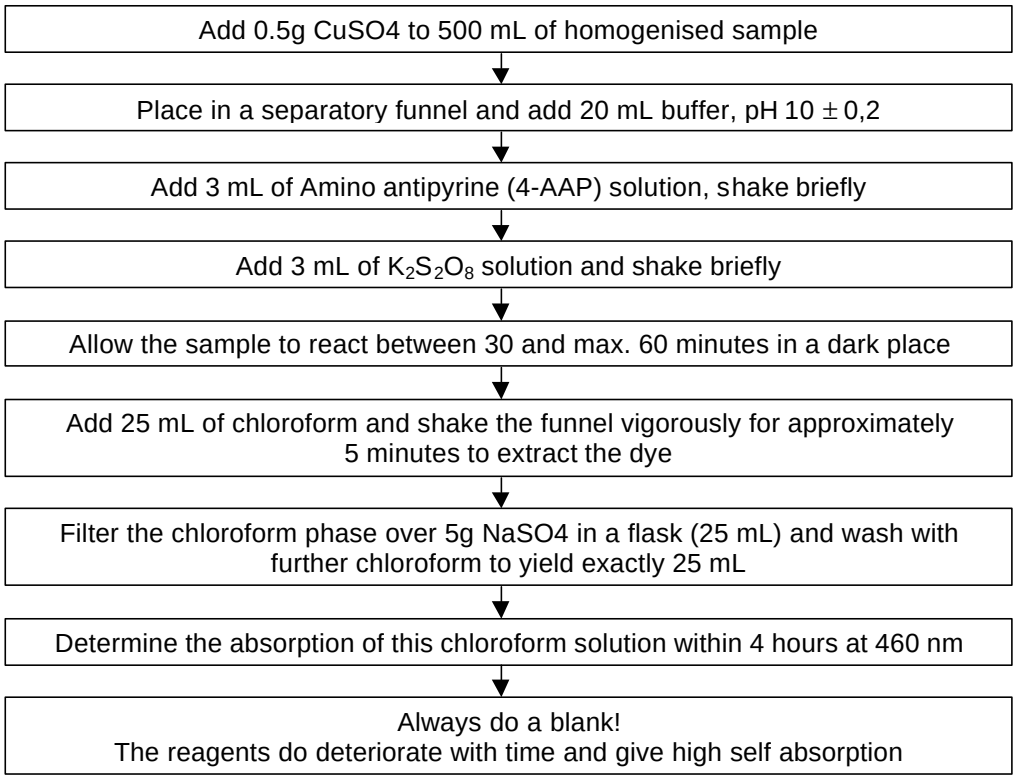


Figure 6: Working procedure as given in DIN 38409- H16/1

The manually determined sum parameter is rather time and labour intensive (Figure 6). Attempts have been made to reduce the manual work involved in the determination of the phenols by the phenolindex. A flow injection analysis is suggested by Frenzel et al. (1992) and Frenzel & Krekler (1995). The first instruments have been introduced in Germany by SKALAR, Erkelenz. Although the manually determined sum parameter already uses large quantities of toxic chemicals, the automated method requires even larger amounts. This increases the cost and furthermore widens the gap between environmental analysis and the production of hazardous waste.

Several attempts have been made to improve (i.e. automate, improve selectivity) the above described standardised sum parameters or replace them by other phenolic group selective parameters. A concise overview of these is reported in the following paragraphs.

Infrared spectroscopy (IR) which is not applicable to water samples but highly attractive for air monitoring, leakage tests and industrial warning systems due to its possibility for directly readable continuous measurement has been suggested by i.e. ETZKORN *et al.* (1999) and (RAJAKOVIC *et al.* (1995)).

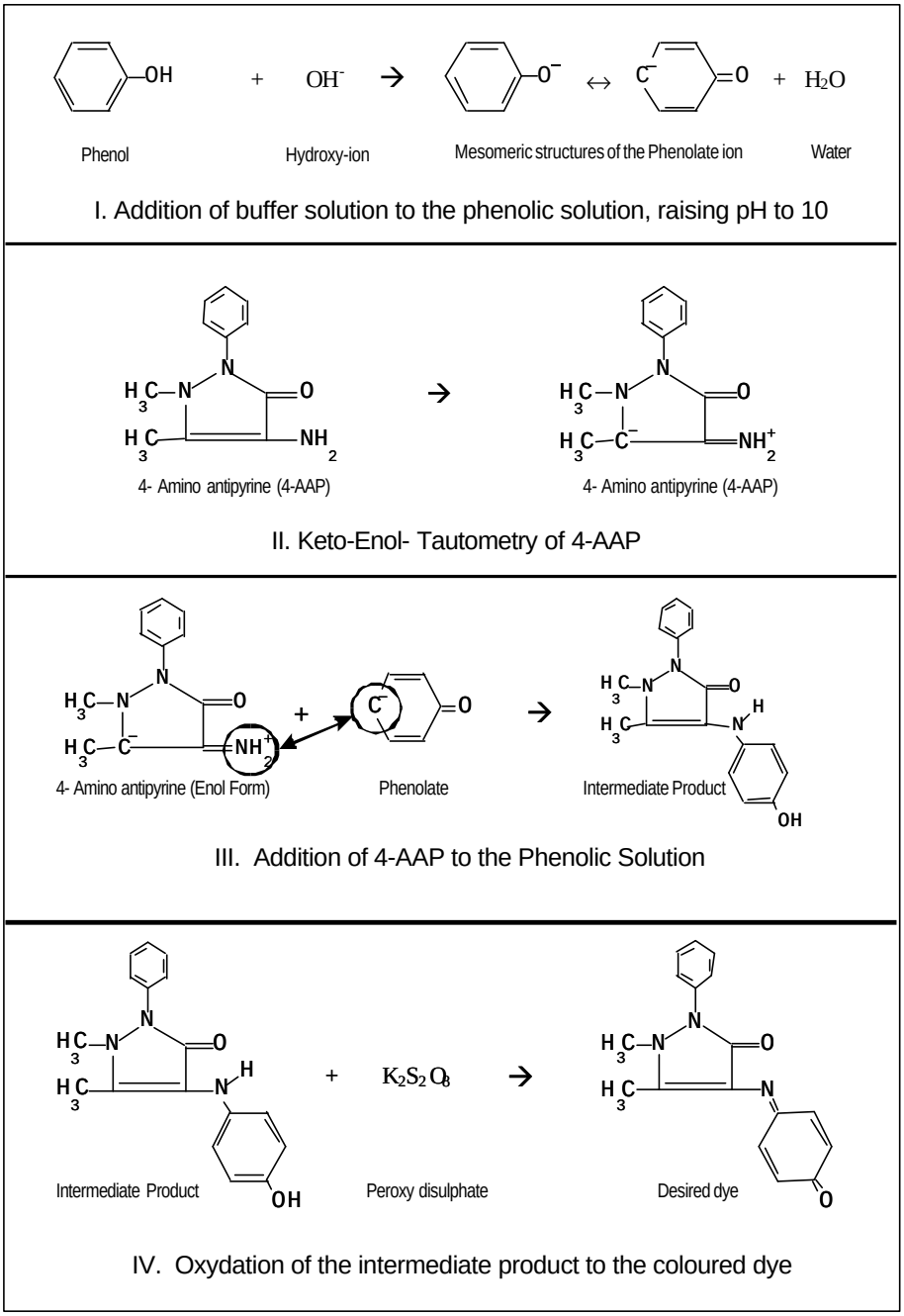


Figure 7: Reaction steps for the phenolindex DIN 38409- H16/1

FOUNTAINE *et al.* (1974) report about a new Ultraviolet Ratio Spectrophotometric System (URS) based on the 4-AAP reaction for the determination of phenolic traces in water samples. Two lamps are used in the URS method. Their difference in adsorption by rising the pH of the sample is assigned to the phenol concentration. The authors conclude that the advantages of the URS method over standardised procedures are: a) it provides more accurate analysis for samples containing para blocked phenols, b) only one reagent is needed, c) it is simple to use and d) analysis can be performed on smaller samples.

The determination of total phenols in waters and wastewater using flow injection with electrochemical detection (FIAS-ED) as reported by CHRISTOPHERSEN & CARDWELL (1996) offers an alternative to the standard colorimetric procedure. More reliable data can be

obtained for samples containing para-substituted phenols and nitrophenols with this method.

Newer developments for the determination of phenols as a sum parameter in water are based on biosensors (RAININA *et al.* (1996), BRECHT & GAUGLITZ (1992), WEI *et al.* (1991)) and sensitive electrodes (GARCIA & ORTIZ (1999)).

Nonetheless, a sum parameter does not account for the significantly different toxicities and properties of the individual phenols (Tab. 4, p. 9). Furthermore, the determination of total phenols neglects valuable information existing in the distribution pattern of individual compounds. Overall, this demands more sophisticated chemical analytical methods which can distinguish between the SCAP and report them as individual compounds.

3.2 Determination of SCAP as individual compounds

A number of methods for the analysis of individual phenols have been published. A summary of those has been reported by e.g. Möder (2000), LÜDERS (1999) and PUIG & BARCELO (1996). These include: liquid chromatography, gas chromatography and capillary zone electrophoresis. Further analytical methods applied to the separation of SCAP include the successful application of open-tubular liquid chromatography (MASKARINEC (1983)) and the application of thin layer chromatography to the acetic esters of phenols (KUNTE (1971)). Chromatography encompasses a diverse and important group of technologies that allow the separation of closely related compounds from complex mixtures, with many of those separations being impossible by other techniques. In all chromatographic separations the sample is dissolved in a mobile phase, which may be a gas (GC, gas chromatography), a liquid (HPLC, high performance liquid chromatography) or sometimes a super critical fluid (SFC, super critical fluid chromatography). The mobile phase is then forced through an immiscible stationary phase, which is fixed in a place in a column or on a solid (analogy: flow through porous media). The two phases are chosen in a manner so that the compounds in the sample distribute themselves between the mobile and the stationary phase at varying degrees. Compounds which are strongly retained by the stationary phase move only slowly with the flow of the mobile phase. Whereas, components that are weakly held by the stationary phase travel rapidly. As a consequence, sample compounds separate into discrete bands that can then be detected by various techniques as individual peaks.

3.2.1 HPLC

LÜDERS (1999) tested various liquid chromatographic methods, different stationary phase such as reversed phases (RP) and normal phases (NP) and several detection systems

including HPLC-MS (HPLC – mass spectrometry) and HPLC-NMR (HPLC-nuclear magnetic resonance). He reports, that SCAP are separated on RP-phases (hydrophobic interactions) according to the number of carbon atoms in the side chain. The more carbon atoms outside the benzene ring of the analyte, the stronger is its interaction with the stationary phase and the longer is its retention time. However, the separation efficiency of RP-phases for positional isomers is rather low since these isomers differ only slightly in their hydrophobicity. He further describes that alkylphenols can be separated on NP-phases with different selectivities. The analytes will be separated on this phase according to their polarity and geometry, but not hydrophobicity. This allows in fact the separation of positional isomers but no longer the distinct separation between C_0-C_3 SCAP. He concludes that both stationary phases result in overlapping peaks.

The application of liquid chromatographic separations is nonetheless a suitable method for aqueous samples with little interfering matrix containing only non interfering SCAP. Such samples are often derived in controlled laboratory studies. They can be directly injected without further treatment (LÜDERS (1999)) and thus greatly improve sample throughput and precision. The identification of phenols using HPLC is further improved by the reaction with *p*-nitrobenzene diazonium tetrafluoroborate as their azo derivatives (KUWATA *et al.* (1981)).

The analysis of coal tar derived phenols in soils by cold extraction with methanol-water and HPLC has recently been standardised in the UK as BS 8855-2:2000. Resorcinol, catechol, phenol, m/p/o cresol, 3.4/2.6/3.5/2.3/2.5/2.4-dimethylphenol, 1-naphthol, 2-isopropylphenol and 2.3.5-trimethylphenol are claimed to be separated isocraticly on a 5 µm octadecyl silica (25 cm x 4.5 mm) with methanol-citric acid/acetate buffer (60:40) and detected by electrochemical oxidation. However, reported retention times are often so close together, that it seems questionable, if the chromatograms can be analysed as individual compounds. Furthermore, the described cold extraction without extract cleaning prior to analysis may add severe matrix interference to the chromatograms. Note that not all SCAP are included in this method. In total, this may lead to misinterpretation of the resulting chromatograms.

BENNETT *et al.* (1996) describe the separation of SCAP in crude oils and water by reversed phase HPLC with sodium acetate buffer/acetonitrile as eluent at pH 11.6. The phenols are fully ionised at this pH and this applied method is comparable to the ion chromatography operation mode. Finally the phenols are detected electrochemically (amperometrically). The major drawback of this method is the extensive peak broadening observed for peaks beyond 4 minutes (i.e. dimethylphenols) which results in loss of sensitivity. C_3 Phenols cannot be determined by this method.

YOSHIKAWA *et al.* (1986) developed a HPLC method utilising beta-cyclodextrin for a complete separation of cresol isomers in urine samples within 16 minutes. With at least 1.5% of β-cyclodextrin in the mobile phase, cresol isomers were separated completely. The optimal amount of beta-CD was determined to be 2.5 g considering relative peak separation and retention time. Detection limits of cresol isomers were about 15 ng. As reported by the authors, this method could unfortunately not successfully be extended to other SCAP.

3.2.2 Gas chromatography mass spectroscopy (GCMS)

Gas chromatography is an excellent method to separate complex mixtures of semi-volatile and volatile organic compounds. Its principle lays in the interaction of the volatilised organic compounds in the gas stream (mobile phase) with the adsorbent compounds on the column walls (stationary phase) resulting in a retardation of the analytes. The different interaction strengths of the individual analytes, as well as their different boiling points causes this separation. Complex samples contain a variety of compounds, which may influence the separation efficiency and could complicate interpretation of chromatograms. Those samples require a preliminary preparation as described in chapter 3.3.

The mass spectroscopic detector allows the very selective determination of analytes by their mass spectra. For the case that only the most intense key ions are monitored (selected ion monitoring, SIM) a very good signal to noise ratio in combination with a good sensitivity can be obtained. Beside this, an MS detector in its various modifications allows e.g. the identification of unknown compounds and the determination of isotopic ratios.

The priority phenols, mainly chloro- and nitrophenols as well as 2.4-dimethylphenol, cresols and phenol have attracted the most attention in the development of analytical methods. Numerous standardised analytical procedures for these priority phenols are available (EPA, METHOD 604 (1984), EPA, METHOD 625 (1984), EPA, METHOD 8040 (1986)). But the analysis of all SCAP in various matrices is only little reported.

The separation of all SCAP by GC is challenging since certain isomers (i.e. m-cresol and p-cresol) show only little variation in their physicochemical properties. Their separation requires a considerable effort. It can be done either by utilising derivatisation techniques, using GCMS in the selected-ion mode (SIM), choosing a specialised or a thick coated capillary column. SCHOMBURG (1987) describes the separation of the 3 cresols and 6 dimethylphenols without derivatisation on a non polar capillary column (OV 1) which however had a film thickness of 0.70 µm. Those columns are not favoured in GCMS.

The development of polar columns on polyethylene glycol basis supported the separation of SCAP. Strong acids often exhibit peak tailing for standard columns. Terephthalic acid

modified polyethylene glycols (DB-FFAP) decrease the amount of tailing and are especially useful for the analysis of phenols (HOSHIKA (1977)). Stabilwax-DA capillary columns and Stabilwax capillary columns have successfully been applied to the analysis of cresols. PENDERGRASS (1994) reports the baseline separation of all cresol isomers. Peak resolution, overall peak shape and precision were improved with the Stabilwax-DA column.

A derivatisation step is commonly included in the sample preparation to achieve the desired separation of the individual phenols. In the following these techniques and their application to the analysis of SCAP is introduced.

Derivatisation

Although derivatisation was not applied in this study its overall importance for the analysis of SCAP by GC expressed by the numerous applications described deserves some introduction.

Derivatisation is used when analytes are either not sufficiently volatile, too strongly attracted to the stationary phases or thermally labile compounds. For SCAP, derivatisation is performed to convert the polar hydroxyl group (active hydrogen atom) into a non-polar group. Consequently, the derivatisation technique reduces the undesirable interactions (i.e. irreversible adsorption) between column and analytes. The disadvantages associated with derivatisation are: a) the derivatisation conditions may cause unintended chemical changes in a compound, b) the derivatisation step may increase the analysis time and c) the derivatisation may complicate the interpretation of non-target screening analysis.

Chemical derivatisation usually involves simple chemical reactions which are likely to result in good quantitative quality. There are many derivatisation reactions, that are used in GC sample preparation. Derivatisation methods can be classified into 4 groups based on the reagents applied and the reaction achieved, namely: **silylation**, **acylation**, **esterification** and **alkylation.** It needs to be assured that the derivatisation is quantitative. Solvents with active hydrogen atoms such as water and alcohols cannot be used. This is why a derivatisation requires prior extraction to transfer the analytes from an aqueous phase to a derivatisation compatible phase.

NANNI *et al.* (1990) reported the successful separation of all 3 cresol isomers in cigarette smoke condensate by derivatisation. A GC method for the analysis of all cresol isomers as their heptafluorobutyrate esters in urine is reported by DILLS *et al.* (1997)). The use of heptafluorobutyric anhydride as derivatising agent furthermore enables the use of an electron capture detector. Chromatographic resolution was achieved between all cresol

isomers and their $2H^7$ analogues. Calibration ranged from 0.001 to 500 µg/mL. Recoveries were 55-97% and showed no trend with respect to analyte concentration. Within-day precision of analyses of benchmark urine samples had a coefficient of variation of less than 4%. DASGUPTA *et al.* (1997) describe a method for urinary phenols using 4-carbethoxyhexafluorobutyryl chloride after extraction from urine and subsequent analysis by GCMS. The derivative elutes at significantly higher temperature than the subsequent phenols which in turn eliminates interferences from volatile compounds. Excellent chromatographic properties of these derivatives were observed with strong molecular ions for the 4-carbethoxyhexafluoro butyryl derivative of phenol (m/z 344), p-cresol (m/z 358) and other characteristic ions in the electron ionisation, thus aiding the unambiguous identification of these compounds (FOGELQVIST *et al.* (1980)). The determination of carboxylic acids and phenols in water by extractive alkylation using pentafluorobenzylation and GC-ECD determination using pentafluorobenzylbromide as alkylating agent is described by HOSHIKA & MUTO (1979). They suggest the conversion of phenol, o-, m- and p-cresol, 2,3-, 2,5-, 3,4- and 3,5-dimethylphenol into their corresponding bromophenols by reaction with Br. The minimum detectable amount of the bromophenols with an ECD was approximately 0.01 ng. However, this method cannot be applied to all matrices.

The most applied derivatisation agent for GCMS or GC-FID determination of phenols is acetic anhydride. BALLESTEROS *et al.* (1990) describe two gas chromatography procedures for the determination of a variety of substituted phenols in water samples. The phenols were extracted or extracted-derivatised by using a continuous liquid-liquid extraction-derivatisation system and quantified with flame ionisation detection. Ethyl acetate was found to be the most efficient solvent for phenols whereas n-hexane yielded essentially the same recoveries for the derivatised phenols. The limit of detection (LoD) is between 0.1 and 300 mg/L for the different phenols at a relative standard deviation between 1.1 and 3.7%. The successful extractive acetylation for SCAP in urine samples resulting in a complete separation of all cresols and dimethylphenols on a Se-54 capillary column was described by WEBER (1992). The overall recoveries of urinary phenols relative to the internal standard, 3-chlorophenol, were in the range 92-99%. The acid hydrolysis of phenol conjugates in urine by concentrated H_3PO_4 followed by the extraction of phenols with n-hexane and their acetylation before gas chromatography on columns packed with OV-1 or OV-17 is reported by BALIKOVA & KOHLICEK (1989). The detection limit is 1 mg/L.

COUTTS *et al.* (1979) report an aqueous derivatisation method for environmental samples. Acetate esters of 6 priority phenols were formed by the direct addition of 500 µL acetic anhydride to 250 mL of a dilute aqueous phenolic solution containing 10 g sodium bicarbonate. In the concentration range of 0.08-0.24 µmol/L, phenol, o-cresol, m-cresol, p-cresol, 2,4-dichlorophenol and l-naphthol easily formed acetate esters which fully separated on an OV-17 or OV-101 column. HARGESHEIMER *et al.* (1984) applied this method

to the analysis of ppb levels of phenolic compounds in waste waters from the Syncrude Canada Ltd. oil sands plant in northern Alberta (Canada). They identified several SCAP whereby only 4 SCAP appeared as individual peaks in the chromatogram.

The use of diazomethane as derivatisation agent is described by LEGA *et al.* (1997). This enables the simultaneous determination of organochlorine pesticides, PCBs, PAHs, phthalates, chloroaromatics, phenolics, phenoxy acids and other base/neutral compounds in environmental samples.

The conversion of SCAP into trimethylsilyl derivatives as a further method for the separation of the cresol isomers has been developed by OYDVIN *et al.* (1966). However, this method requires the addition of tri-o-cresyl phosphate to the stationary phase in order to separate all SCAP. The method was further developed and applied by ISHIGURO & SUGAWARA (1978) and WITTKOWSKI *et al.* (1981) for the simultaneous analysis of SCAP in tobacco smoke condensate. It has further been applied to the microanalysis of aqueous samples for phenols and organic acids by PRATER *et al.* (1980). Trace concentrations in the parts-per-billion levels of these water pollutants were determined which is accomplished by a concentration step using macroreticular resins with pyridine elution and subsequent derivatisation with bis-trimethylsilyl acetamide.

A method for the nearly fully separated analysis of SCAP as their ferrocenecarboxylic acid esters by CG-AED (atomic emission detector) in crude oil has been described by ROLFES & ANDERSSON (2001). This method is easy applicable for the analysis of SCAP in crude oil. However, the AED is not a common detector in GC which makes this method less favourable in practise.

The most commonly applied derivatisation agents for phenols are summarised in Tab. 10.

Tab. 10: Summary of typical derivatisation reagents applied to phenols (MÖDER (2000))

Reagent	CAS No.	Transferred group	Analysis by
Trimethylsilylation			
Bis(trimethylsilyl)acetamide	10416-59-8	$(CH_3)_3Si$	GC / FID, MS
Bis(trimethylsilyl)trifluoroacetamide	25561-30-2	$(CH_3)_3Si$	GC / FID, MS
Trimethylchlorosilane	75-77-4	$(CH_3)_3Si$	GC / FID, MS
1,1,1,3,3,3-Hexamethyldisilazane	999-97-3	$(CH_3)_3Si$	GC / FID, MS
N-(Trimethylsilyl)diethylamine	996-50-9	$(CH_3)_3Si$	GC / FID, MS
N-(Trimethylsilyl)imidazol	18156-74-6	$(CH_3)_3Si$	GC / FID, MS
Acylation			
Heptafluorobutyric anhydride	336-59-4	C_3F_7CO	GC / ECD, MS, FID
N-[Methyl-bis(trifluoroacetamide)]	685-27-8	CF_3CO	GC / ECD, MS, FID
Trifluoroacetic anhydride	407-25-0	CF_3CO	GC / ECD, MS, FID
Acetic anhydride	108-24-7	CH_3CO	GC / FID
Alkylation			
Pentafluorobenzyl bromide	1765-40-8	$C_6F_5CH_2$	GC / ECD, MS, FID

Introducing cyclodextrin GC-phases

Cyclodextrin based capillary columns in the gas chromatographic separation have been reported to be an excellent stationary phase to separate not only enantiomers but also positional isomers (BECK *et al.* (2000), MIRANDA *et al.* (1998)). Its application in this study as the stationary phase material to the separation of SCAP demands some introduction to this type of column.

There are three native cyclodextrins (alpha, beta and gamma cyclodextrin indexed by the prefix A, B and G) used as their derivatives as stationary phase additive in capillary gas chromatography. They differ in size and are derivatised by various groups at varying degrees thus allowing the separation of a wide variety of analytes. This additive can be dissolved in the stationary phase which is bonded to the fused silica or is itself bonded to the fused silica. Selectivity of these phases is a function of the derivative, the degree of derivatisation as well as the position of the derivative on the cyclodextrin. Seven phase types, each with either alpha, beta or gamma cyclodextrin, are commercially available. Most important for the separation of positional isomers seem the DA/DM/PH/PM phases in which the separation is caused by inclusion effects and H-bonding. The choice of the cyclodextrin determines the size of the analytes to which the stationary phase is most selective. Major drawbacks of inclusion dominated separations are a lower analyte capacity due to fewer interaction sites as compared to a surface interaction dominated mechanism. This limits the calibration range to only two orders of magnitude maximum.

Non bonded cyclodextrin columns are very sensitive towards moisture and oxygen which can both affect the columns selectivity and stability. Dry carrier gas, oxygen traps and the injection of virtually water free samples are essential for continued optimum performance. These columns have a very limited temperature operating range which should not be more than 220°C for most applications. Additionally, the heating rate or cooling down rate should not be more than 10°C/min. Otherwise the stationary phase may deteriorate more rapidly.

Bonded cyclodextrin phases are bound the fused silica together with the non-polar phase (5% Phenyl/95% Methylpolysiloxane). This makes them more robust towards water traces. Their separation is almost only caused by cyclodextrin. This may be an advantage for the separation of optical isomers but not really for the separation of positional isomers with polar nature (Chrompack Application Note #1449, Figure 8). Those analytes appear in extremely broad peaks since the non-polar phase can not work against the dispersion and diffusion and thereby sharpening the peaks. Figure 8 shows the opportunities existing with such columns for the underivatised separation of SCAP.

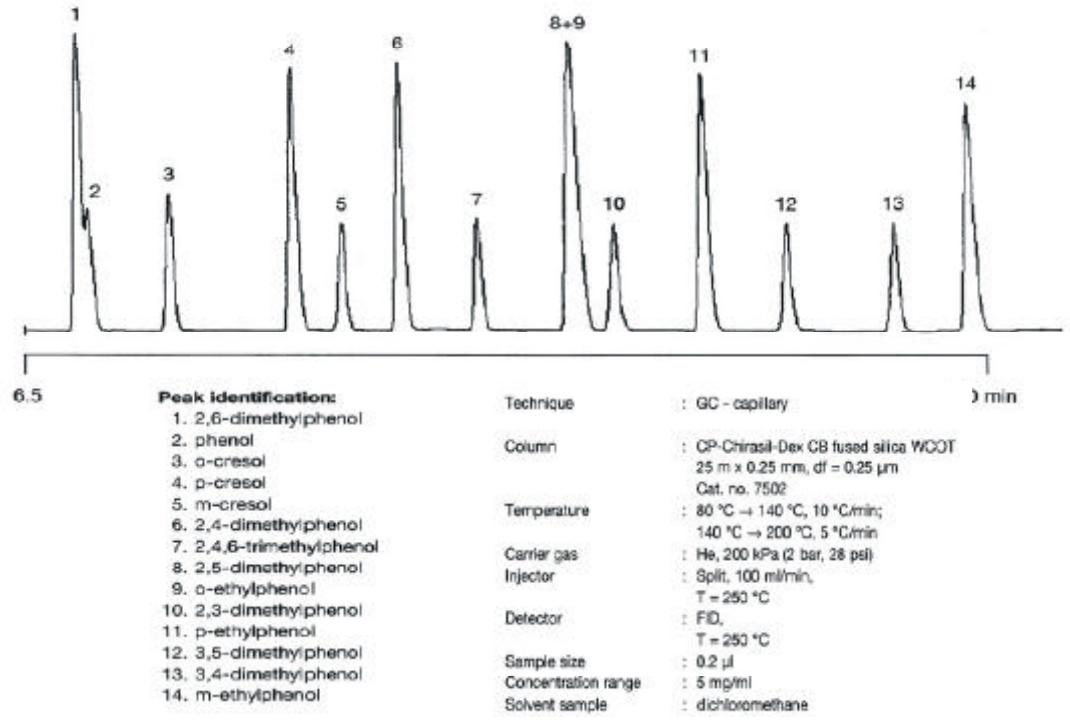


Figure 8: Bonded cyclodextrin column, Application #1449 Chrompack[7]

Cyclodextrin columns should best be operated with hydrogen or helium, which are gases with high diffusion coefficients. The inclusion mechanism is based on diffusion and back diffusion mechanisms which result in rather broad peaks. The term A in the van Deemter equation for such columns becomes predominant resulting in a very flat van Deemter curve. A possibility can be an increased flow rate to minimise peak broadening. Such columns are often operated with approximately 20-30 kPa higher front inlet pressures. The vacuum conditions in the MS detector however often limit the maximum flow to around 2 – 4 mL/min.

3.3 Sample preparation methods as applied to phenols

Sample preparation is as important as sample analysis. If the sample is ill prepared, the analysis can be incorrect. Main aspect of the sample preparation are e.g. minimising interferences by matrix reduction and the enrichment of analytes. The preparation of aqueous samples usually begins with the enrichment of the organic analytes by any of the following procedures: liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase micro extraction (SPME), Purge and Trap (P&T) or headspace sampling, solid

[7] Own trials gave a different elution order under identical conditions.

phase dynamic extraction (SPDE, MUSSHOFF *et al.* (2001)), stir bar adsorptive extraction (TWISTER®, POPP *et al.* (2001), BALTUSSEN ET AL (1999A), BALTUSSEN *et al.* (1999B)) or headspace solvent micro extraction (THEIS *et al.* (2001)). The most commonly applied extraction procedures for solid and aqueous environmental samples are summarised in Figure 9.

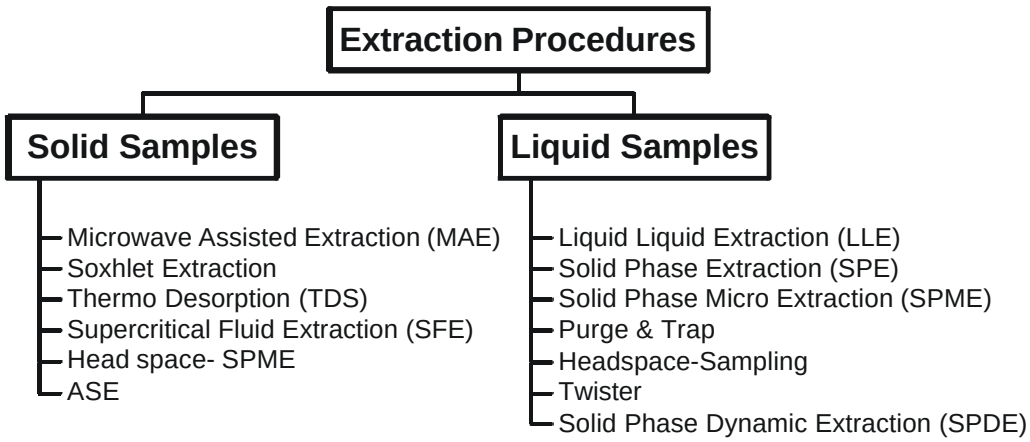


Figure 9: Overview of most commonly applied extraction procedures

Favoured extraction methods for solid samples include Soxhlet extraction, microwave assisted extraction (MAE), accelerated solvent extraction (ASE, WENNRICH *et al.* (2000)), supercritical fluid extraction (SFE, LI *et al.* (1998B), RAMSEY *et al.* (1997), REIGARD & OLESIK (1996), YUAN & OLESIK (1997)), thermo desorption (TDS, GERSTEL APPLICATION NOTE 02/1994, PEREZ-COELLO *et al.* (1997)) and SPME from headspace at elevated temperatures (BACIOCCHI *et al.* (2001), LEE *et al.* (1998)). All of the above listed sample preparation methods have their advantages and disadvantages as well as their field of application in which they are most selective.

3.3.1 Liquid-liquid extraction (LLE)

Although not applied in this study, LLE is as one of the more commonly used forms of sample preparation widely applied to SCAP in routine analysis (MÖDER (2000), EPA, METHOD 604 (1984), EPA, METHOD 625 (1984)).

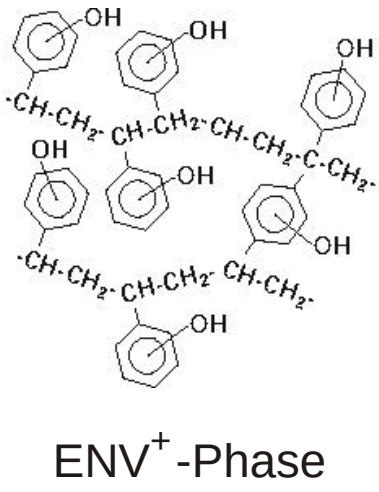
Liquid-liquid extraction is a separation process that takes advantage of the relative solubilities of solutes in immiscible solvents. It is generally used to a) separate analytes selectively from matrices b) move components from a method incompatible into a method compatible solvent i.e. for gas chromatography from a less volatile liquid into a more volatile liquid or c) provide better conditions for derivatisation. The distribution coefficient determines the ratio of the solute's concentration in each solvent (ROBBINS (1980)). Due to the high water solubilities of phenol and cresols this coefficient is rather small, suggesting that LLE cannot directly be applied to the selective enrichment of those SCAP (HRIVNAK &

STEKLAC (1984)). It is however applicable to their acetic ester derivates (HARGESHEIMER *et al.* (1984), JUSI & LIHUI (1992)) .

Overall, LLE is rather time and labour intensive. An extraction procedure with extract clean up and volume reduction can easily require 2 to 5 hours per sample. Besides, LLE requires large amounts of sample and of organic solvents. Therefore, this extraction method has not been considered during the SCAP method development.

3.3.2 Solid-phase extraction (SPE)

SPE is an extraction method based on adsorbent extraction and back elution of analyte into a small volume of solvent. From a variety of adsorbent phases (AMBROSE *et al.* (1997), SUN & FRITZ (1992)) the most selective for the extraction problem can be chosen allowing a wide application range for this method (MENEY *et al.* (1998), SUPELCO (1998), TORIBIO *et al.* (1998) SONG *et al.* (1997), KOCH & VÖLKER (1995)). Several extraction procedures for EPA-Phenols and some SCAP are described (DUPEYRON *et al.* (1995), MASQUE *et al.* (1998), MUßMANN *et al.* (1994)). Phenols, as polar compounds, are best extracted on hydroxylated polystyrene-divinylbenzene phases (ENV+,Figure 10). A commercially available SPE system as routinely applied in praxis is shown in Figure 10. The cartridges containing the adsorbent are placed onto the manifold and the sample is applied on top of these cartridges. An adjustable negative pressure applied to the manifold ensures a constant flow rate during extraction. Although, the manifold allows to extract 10 samples simultaneously, practically this seems rather impossible.



ENV$^+$-Phase

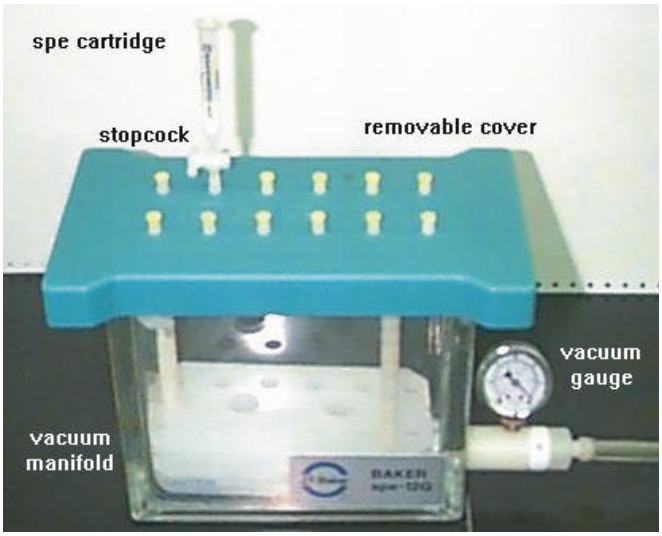


Figure 10: ENV as a adsorbent for phenols[8] (left), illustration of a SPE set-up[9] (right)

3.3.3 Solid phase micro extraction (SPME) [10]

The development of this solvent free extraction technique offers a simple way of analyte enrichment from environmental samples. Based on sorption processes this technique combines sampling, extraction, analyte enrichment and even injection into a single device. SPME is a major breakthrough in chemical analysis and significantly decreases the cost as well as the time needed for sample preparation for the main chromatographic methods like gas chromatography and HPLC (BOYD-BOLAND & PAWLISZYN (1996)).

The SPME device consists of a thinly coated (20-100 µm of a polymer adsorbent) fused silica fibre attached to a stainless steel plunger and installed in a holder with the fragile fibre mechanically protected by a hollow needle. The general work procedure of SPME is illustrated in Figure 11. In the first step the device with the retracted fibre passes through the sample vial septum. Then the plunger is pushed to expose the fibre within the vial, and extraction starts as organic analytes adsorb at the coating on the fibre. Hereby, sample agitation enhances extraction thus reducing the extraction time. After a set time the fibre is retracted into the needle and the device withdrawn from the vial. Finally, the needle of the device is introduced into the injector of the chromatographic system, where the analytes

[8] http://www.argotech.com/products/spe_columns/resin.html - 23.05.2002
[9] http://www.chem.vt.edu/chem-ed/sep/extract/spe.html - 25.05.2002
[10] http://info.sial.com/Graphics/Supelco/objects/4600/4547.pdf - 30.06.2002

are made to desorb from the fibre.

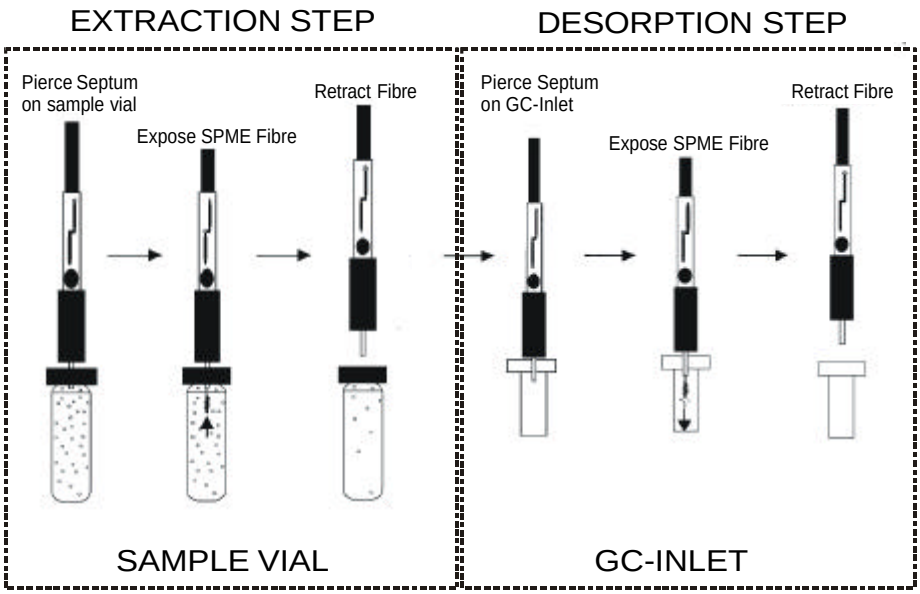


Figure 11: Illustration of the SPME procedure [11]

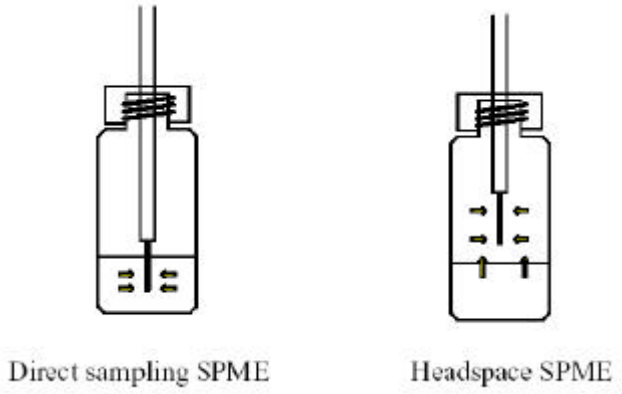


Figure 12: Headspace sampling vs. Direct immersion (Direct sampling)[12]

Two SPME modes exist: a) direct immersion of the fibre to the sample and b) sampling the headspace above the sample (Figure 12) which have been both considered complementary (YANG & PEPPARD (1994)). Depending on the vapour pressure of the analyte either method is favoured. If extracting the analytes by using an immersion sampling technique, minimising the headspace in the sample vial is vital while the opposite applies to analytes that accumulate in the headspace. Increasing the sample volume while keeping the liquid to headspace ratio constant increased analyte adsorption by either

[11] http://info.sial.com/Graphics/Supelco/objects/4600/4547.pdf - 24.06.2002
[12] http://www-fst.ag.ohio-state.edu/min/IFT-SPME-2000.ppt - 25.06.2002

immersion or headspace SPME (YANG & PEPPARD (1994)). For higher sensitivity from headspace SPME, the sample headspace should be as small as possible in a practical sense (ZHANG & PAWLISZYN (1993)). Direct immersion of the fibre to a prepared sample (acidified and salt added) dramatically decrease the performance of the fibre. As shown by Möder et al. (1997), salt inactivates the fibre during the desorption step in the GC injector since it bakes onto the fibre during desorption because of the high temperature applied. Under most conditions, an assembly can provide 50 to 100 extractions in direct immersion mode and up to 500 extractions in headspace mode.

In SPME, equilibria are established among the concentrations of an analyte in the sample, in the headspace above the sample, and in the polymer coating on the fused silica fibre. The amount of analyte adsorbed by the fibre depends on the thickness of the polymer coating and on the distribution constant for the analyte. The extraction time is determined by the time required to obtain precise extractions for the analytes with the highest distribution constants. The distribution constant generally increases with increasing molecular weight and boiling point of the analyte.

For SPME coatings, the amount of analyte adsorbed by the coating at equilibrium is directly related to the concentration of the analyte in the sample (ZHANG *et al.* (1994))[13]:

$$n = \frac{K_{fs}\, V_f\, V_s}{K_{fs}\, V_f + V_s} \cdot c_0$$

where n is the mass of analyte adsorbed by coating, c_0 is the initial concentration of analyte in sample, K_{fs} is the partition coefficient for analyte between coating and sample matrix, V_f is the volume of coating and V_s is the volume of sample

If V_s is very large, the amount extracted by the fibre coating is no longer related to sample volume which makes SPME suitable for field sampling (GORECKI & PAWLISZYN (1997)). The selectivity of SPME can be altered by changing the type of polymer coating on the fibre, the coating thickness, the extraction/desorption temperature, the sampling mode as well as the pH and the ionic strength of the sample. Saturating the sample with sodium sulphate increases the ionic strength of the solution and in turn can reduce the solubility of some analytes (SETSCHENOW (1889)). This effect only little applies to analytes with high distribution constants and polar compounds such as SCAP. Phenols are more effectively

[13] K_{fs} values usually are not sufficiently large to exhaustively extract the analyte from the matrix.

extracted under acidic pH. A combination of salt and pH modification often enhances the extraction of analytes from headspace.

Results of SPME generally compare very favourably to results from other sample preparation methodologies (PAWLISZYN (1997)). For high accuracy and precision from SPME, consistency in sampling time and all other SPME parameters is more important than full equilibration. For most applications a linear relationship for a wide concentration range is observed (e.g. ARTHUR *et al.* (1992A), ARTHUR *et al.* (1992B), ARTHUR *et al.* (1992/93), GILL & BROWN (2002)).

The desorption step in the injector of the chromatographic system is an important parameter for peak resolution and peak width. Since in GC the desorption is done thermally the desorption of an analyte from a SPME fibre depends on the boiling point of the analyte, the temperature of the injection port and the thickness of the coating on the fibre. Additionally, an inlet liner with a narrow internal diameter (e.g., 0.75mm ID, compared to conventional 2mm ID liners) sharpens the peaks (LANGENFELD *et al.* (1996)).

SPME has been successfully applied to the enrichment of polar compounds from water samples (MATISOVA *et al.* (1999)) including EPA-Phenols BUCHHOLZ & PAWLISZYN (1993) and BUCHHOLZ & PAWLISZYN (1994). The selective enrichment of chloro- and nitrophenols from rather complex matrices by using a polyacrylate fibre has been described in greater detail by MÖDER *et al.* (1997). They discuss the SPME parameters together with their respective advantages and disadvantages and overall suggest the enrichment of those phenols in direct immersion mode from sodium chloride saturated and acidified (pH 2) samples. They suggest the addition of a surrogate internal standard to overcome this drawback. The application of this internal standard yields the precision and accuracy required even at the presence of dissolved natural organic matter (NOM) as shown by PÖRSCHMANN *et al.* (1998).

BARTAK & CAP (1997) investigated the extraction efficiency of EPA-Phenols from the headspace above the sample. They report that a polyacrylate fibre has a significantly higher extraction efficiency for underivatised phenols from headspace than a polydimethylsiloxane fibre has. The conditions for reproducible data by HS-SPME are a) NaCl saturation of the sample, b) addition of HCl to a pH about 1 and c) an extraction time of 60 minutes. They assigned the long extraction time required to the fact that the analyte diffusion into the solid polyacrylate fibre is rather difficult. For that reason, the analyte desorption time was also increased to 8 min. The lack of reproducibility by applying the HS-SPME mode when working under non-equilibrium conditions has been critically mentioned. Further investigations on headspace sampling of polar and/or semi-volatile compounds have been reported by DE LA CALLE GARCIA *et al.* (1998) and HELALEH *et al.* (2001). The latter successfully applied this sampling mode to aqueous solutions of C_9-

C_{12} alkylphenols.

3.3.4 Soxhlet extraction [14]

The soxhlet extractor is one of the most widely used apparatuses to extract organic compounds from solids by solvents. The solid samples are weighed into thimbles, covered with glass wool and placed into the soxhlet chamber. The round bottom flask containing an organic solvent is heated to create enough vapour pressure to produce a steady flow of liquid drops from the condenser at the top into the soxhlet chamber. Once the solvent in the soxhlet chamber rises above the relief arm, the solvent is returned to the round bottom flask and the process repeats itself. Most extractions require one day. Since heat is constantly applied to the bulk solution degradation of thermally labile compounds, favour oxidation processes, polymerisation loss of analytes may be caused. Ultra-pure solvents must be used with each extraction requiring up to 250 mL (PEREZ-COELLO *et al.* (1997)). The large solvent volume produces rather dilute extracts that need to be concentrated before analysis which often contributes to poor recovery.

The application of soxhlet extraction to EPA-Phenols from soil has been described by ALONSO *et al.* (1998). Despite many successfully described recoveries using soxhlet extraction for a broad range of compounds, the long extraction time reduces sample throughput and makes soxhlet extraction an unattractive technique especially when a large number of samples must be analysed or when analytical data are quickly required as in clinical emergency screening.

3.3.5 Microwave assisted extraction (MAE)

The characteristic of microwave extraction (MAE) is accelerated dissolution kinetics as a consequence of the rapid heating processes that occur when a microwave field is applied to a sample. Since SALGO & GANZLER (1986) published applications using a conventional microwave oven to enhance extraction of organic compounds from solid matrices such as soils, seeds, food and feeds this method has been established in most routine laboratories. The technique exploits the Arrhenius relationship of temperature to rate of desorption which is the increased mass transfer as a result of higher temperatures. The heating associated with MAE allows the solvent to rapidly overcome matrix effects and

[14] http://www.instrumentalchemistry.com/sampleprep/pages/soxhlet.htm 02.07.2002

promotes faster desorption of the target analytes and other extractables.

Currently, there are two types of microwave extractors that are commercially available: a closed-system (Figure 13, applied here) and an open-vessel system. The main parameters to be considered for method development in a closed-system are solvent, temperature, pressure, power applied and the extraction time. This system operates under controlled pressure and allows the temperature of the solvent to be raised above its boiling point. Most closed-vessel systems can extract up to 24 samples simultaneously, which greatly increases sample throughput. The extraction efficiency may be determined by the sample size since the energy is split between the extraction vessels. This can reduce the heating rate of the solvent when not compensated by increasing the extraction time or power.

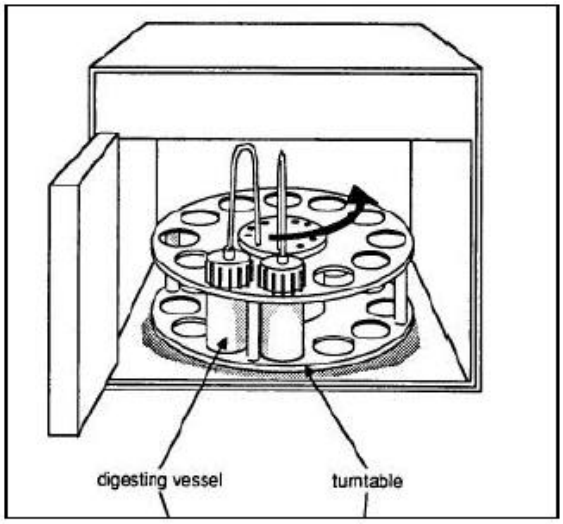


Figure 13: Design of closed-vessel system microwave [15]

MAE has mainly been used to isolate polar components from complex matrices since the solvent must be polar to excitable by the microwaves. ALONSO *et al.* (1998) and HANCOCK & DEAN (1997) report the successful application of MAE to the extraction of phenol from various solids.

[15] http://scholar.lib.vt.edu/theses/available/etd-060899-161452/ unrestricted/Diss.pdf 30.06.2002

4 Method development for SCAP-analysis

The precise and accurate analysis of any pollutant is a fundamental requirement for the monitoring at contaminated sites. This is especially crucial when a monitored natural attenuation (MNA) scheme is employed at a site. It implies that SCAP should rather be analysed as individual compounds than as a sum by an index parameter.

The first subchapter describes the detectability of SCAP by the sum parameter *phenolindex.* The results are presented in terms of their implication for such contaminations in the subsurface.

The next chapters outline the development of an analytical method to determine individual SCAP concentrations in environmental samples. Within the stage of method development the recently introduced *British Standard* (BS 8855-2:2000) for soil samples based on ultrasonic extraction and HPLC was evaluated for its application to the analysis of all SCAP in water samples. In contrast to existing methods for the analysis of SCAP as individual compounds (compare chapter 3.2, pp. 19), which require elaborate extraction and derivatisation steps, an easier method has been developed and is described.

4.1 Phenolindex

The systematic characterisation of the sensitivity and selectivity of SCAP on the *phenolindex* as well as the systematic quantification of this sensitivity are presented in this chapter.

4.1.1 Experimental

Standard stock solutions of 18 SCAP (phenol, o/m/p cresols, 2.3/2.4/2.5/2.6/3.4/3.5-dimethylphenol, 2.4.6/2.3.5/3.4.5/2.3.6-trimethylphenol, o/m/p ethylphenols and o-tertbutylphenol and p-chloro phenol) each with a concentration of 1000 mg/L were prepared in dionised water (18 MΩ, 4 µg/L TOC) by accurately weighing in the pure substances. The stock solutions of 100 mL were stored at 4°C in the dark. The *phenolindex* was determined according to DIN 38409/H16-1. A detailed description of the work procedure can be found in chapter 3.1, pp. 15. Reactant solutions and adequate dilutions of the standard stock solution were prepared according to the DIN procedure.

Dilutions of the standard stock phenolic solutions to 800 µg/L were prepared for the characterisation of the sensitivity of individual alkylphenols towards the *phenolindex*. To quantify their contribution, subsequent dilutions of 100 µg/L were used. The resulting UV-VIS absorption spectra were always recorded in the range of 385-585 nm.

4.1.2 Results and discussion

The experimental results of the characterisation experiments are presented as UV-VIS spectra (385-490 nm) of selected alkylphenol-AAP dyes and shown in Figure 14-Figure 16.

Figure 14 shows the influence of one methyl group at the three possible sites on the ring towards the observable absorption. The intensity at the determination wavelength of 460 nm decreases from 76% for o-cresol to nearly zero for p-cresol. This implies that para alkyl substituted phenols may not form this dye under these conditions. This is in accordance with the reaction pathway (Figure 7, p. 18). Figure 15 shows the effect of an increasing chain length in ortho position. The intensity at the determination wavelength of 460 nm decreases from 76% for o-cresol to nearly zero for 2-tert-butylphenol. This implies that C3 phenols may not contribute much to the *phenolindex* and it must be concluded that the higher alkylphenols such as endocrine disrupters (nonylphenol) can not be detected by this parameter. Figure 16 shows the dependency of varying the number of methyl groups on the ring on the observable absorption at 460 nm. It is clearly visible that the intensity for dimethylphenols and trimethylphenols is rather low. Their real concentration in a sample will not be accounted for in the *phenolindex*.

Generally, the observed absorption intensities at the determination wavelength of 460 nm are rather different. Non of the short chained alkylphenols show a higher sensitivity towards this test than phenol itself. The *phenolindex* does not indicate the presence of para alkyl substituted SCAP. The other SCAP are detected with a significantly decreased sensitivity. Hydroxy and dihydroxy phenols and their alkyl derivatives are excluded from this index since their dyes can not be extracted into chloroform (EMERSON (1943)).

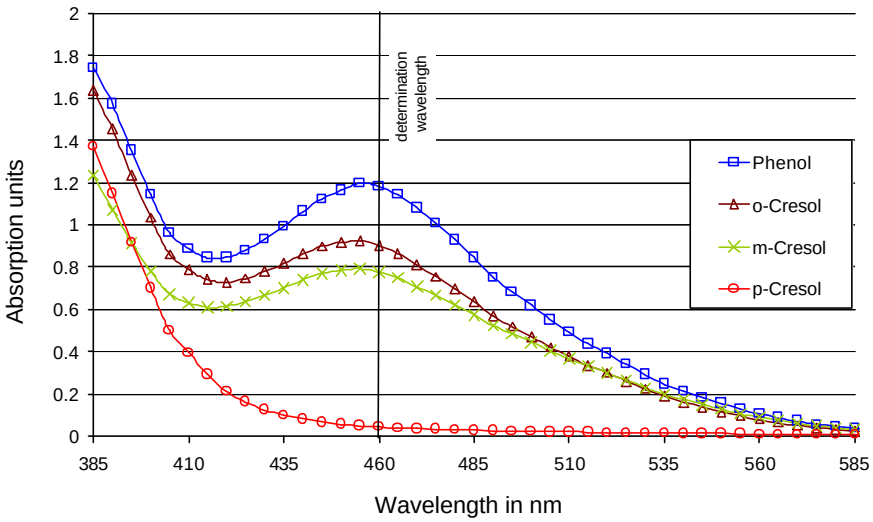


Figure 14: Influence of the position of a methyl group on absorption

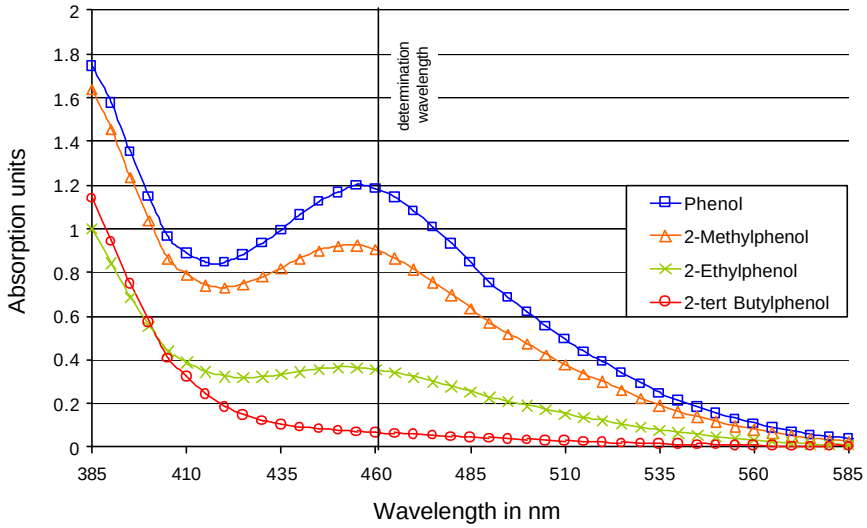


Figure 15: Influence of the chain length on absorption

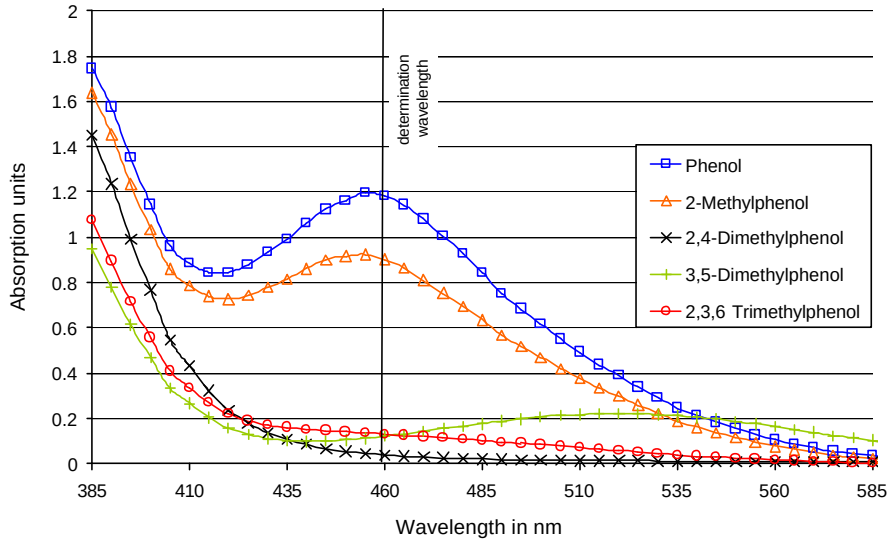


Figure 16: Influence of the number of methyl groups and their position on absorption

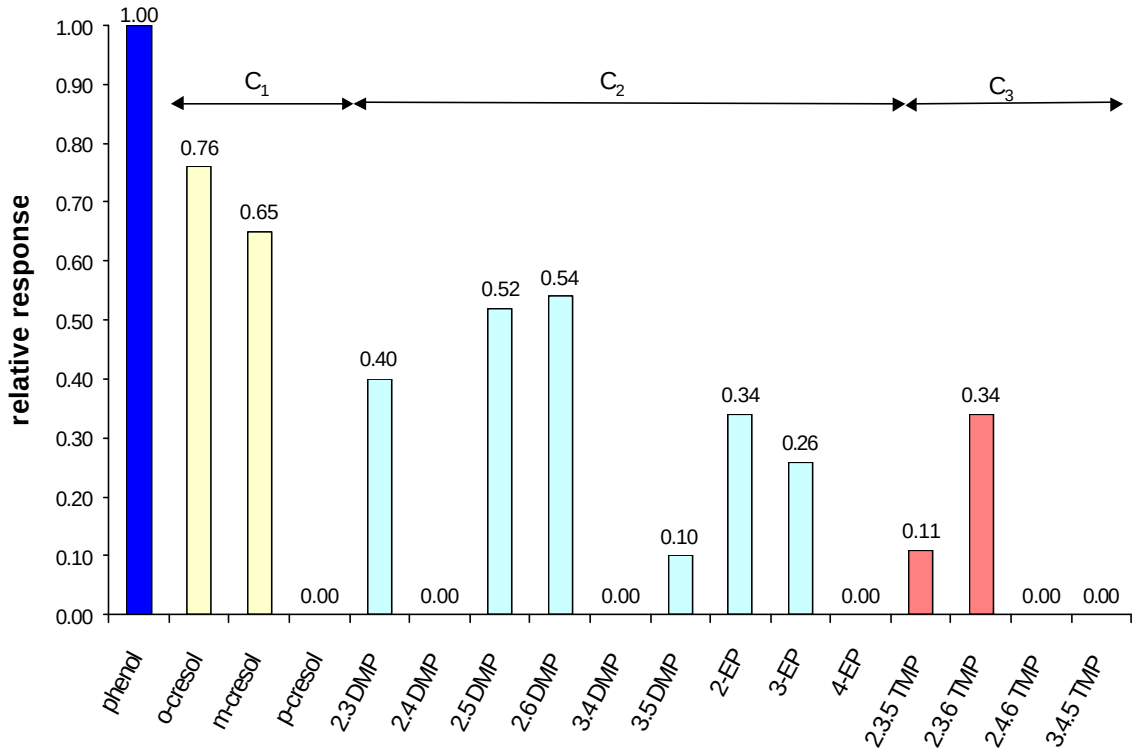


Figure 17: Sensitivity factors for selected SCAP determined by applying DIN 38409/H16-1

It appears that a methyl group in meta position leads to a greater quenching effect than one in ortho position (compare UV-VIS spectra). This effect also applies to dimethyl- and trimethylphenols. However, signal quenching is not the only artefact that may lead to the tremendously decreased sensitivity. The calibration of the *phenolindex* is mass based and done with phenol only (i.e. µg/L). Phenol has the lowest molecular weight within the group of SCAP since each substituent increases the molecular weight of the compound. Consequently, this leads to a discrimination of the C1-C3 SCAP since Lambert Beer's law applies to UV-VIS determinations. In other words, at the same mass concentration a dimethylphenol solution contains 23 % less molecules than a phenol solution does (Figure 18). The maximum observable readout for a dimethylphenol solution will never be more than 77 % of the phenol solution with the same mass concentration (i.e. µg/L). This will be called molecular threshold value. For cresols this value is 87 % and for trimethylphenols it is 69 %, respectively. However, since all observed signals are well below the molecular threshold value, the remaining signal depression must be assigned to quenching effects mainly due to the +I effect of methyl group substituents on aromatic systems and also due to different extinction coefficients for the various 4-AAPdyes.

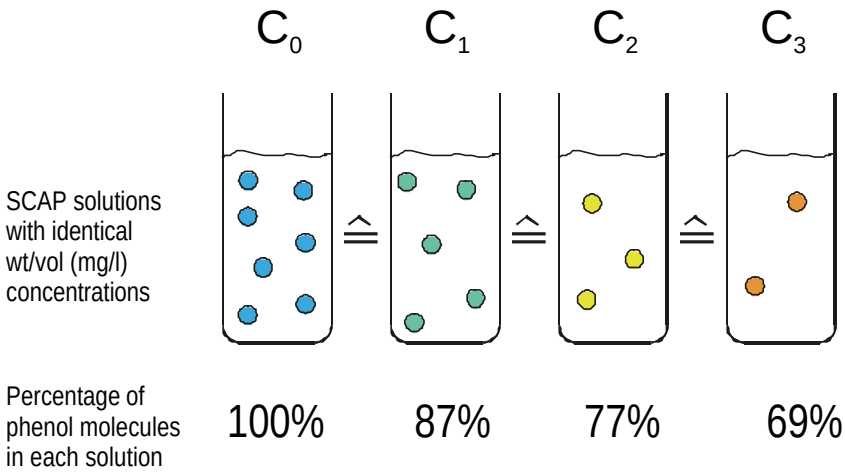


Figure 18: Simplified sketch of molecular concentration vs. weight concentration

To investigate whether the individual sensitivity factors also apply to a mixture of SCAP, a synthetic SCAP solution was freshly prepared. This aqueous solution contained 106 µL certified Phenol-MIX 1 (14 SCAP in methanol, each 50 ng/µL, Dr. Ehrendorfer) in 500 mL de-ionised water (Tab. 11).

Tab. 11: Calculated *phenolindex* vs. experimentally determined[16]

SCAP	Sensitivity Factor	Concentration in prepared sample	Calculated *phenolindex* in µg/L
Phenol	1.00	10.6	10.6
o-Kresol	0.76	10.6	8.06
m-Kresol	0.65	10.6	6.89
p-Kresol	0.00	10.6	0.00
2.3 DMP	0.41	10.6	4.30
2.4 DMP	0.00	10.6	0.00
2.5 DMP	0.53	10.6	5.61
2.6 DMP	0.54	10.6	5.72
3.4 DMP	0.00	10.6	0.00
3.5 DMP	0.10	10.6	1.06
2.4.6 TMP	0.00	10.6	0.00
2.3.5 TMP	0.11	10.6	1.21
3.4.5 TMP	0.00	10.6	0.00
2.3.6 TMP	0.35	10.6	3.66
		CALCULATED	**47.11**
		EXPERIMENTALLY DETERMINED	**48.64**

[16] Multiplication of the sensitivity factor in column 2 by the concentration in the prepared sample in column 3 yields the calculated phenolindex value in column 4 for each SCAP. By adding all calculated phenol values in column 4 the theoretically calculated phenolindex value of 47.11 is obtained.

The *phenolindex* (DIN 38409/H16-1) was immediately determined from that solution. The results are summarised in Tab. 11. Applying the earlier determined sensitivity factors (Figure 17) the *phenolindex* was calculated for each SCAP. Finally, their individual contribution is added which yields a calculated *phenolindex* of 47.11. The determined *phenolindex* value was in fact 48.6 µg/L. This is in good agreement with the calculated *phenolindex* implying that the sum parameter is of incremental nature.

To emphasise the exceptional role that must be assigned to SCAP, the *phenolindex* was performed on a freshly prepared p-chlorophenol solution (100 µg/L). The readout was 72 µg/L (i.e. 72%). This equals the molecular threshold value implying that para-chlorophenol does not belong to the para blocked phenols. Consequently, SCAP are among the toxic phenols probably the least able phenols to be detected by the *phenolindex*.

4.1.3 Implications

The results from the previous section show that SCAP are underrepresented by the *phenolindex*. This implies that the real concentration of these phenols must always be higher than indicated by the sum parameter. To investigate whether this assumption can be generalised, samples from a contaminated site (Rositz, 7.2, p. 102) were taken and analysed within 24h. The individual SCAP compounds were determined by GCMS as outlined in chapter 4.3. and the *phenolindex* was determined in accordance with DIN 38409/H16-1. The results, summarised in Tab. 12 and Figure 19, show that the finding gained from laboratory experiments carried out on synthetic samples could not directly be transferred to field samples. As shown in Figure 19, the analysed *phenolindex* is almost twice as high as the calculated one. The analysed *phenolindex* for well 2 (Tab. 12) seems to be comparable to the total SCAP concentration and for well 3 (Tab. 12) the least expected mismatch applies. All possible deviations between *phenolindex* and total SCAP concentration could be observed on those 3 wells. This can only be explained when other compounds will also give an absorption signal at 460 nm. However, it is rather unlikely and confirmed by own experiments that compounds are present in these samples which can absorb at 460 nm in their chloroform extracts to such an extent. One possible explanation is that those interfering compounds must also undergo some reaction; either with 4-AAP or due to the pH-shift. The formed products must than be extractable into chloroform and show some absorption at 460 nm. Likely candidates which can perform this reaction and fulfil the requirements are heterocyclic compounds and anilines. These compounds are always associated with SCAP (ZAMFIRESCU (2000)). Anilines for example can not even be removed by steam distillation as suggested in DIN 38409/H16-2.

Tab. 12: Comparison of *phenolindex* with total SCAP at 3 wells

µg/l	Well 1	Well 2	Well 3
Total SCAP by GCMS	825.7	128.4	48.6
analysed *Phenolindex*	521	130	257

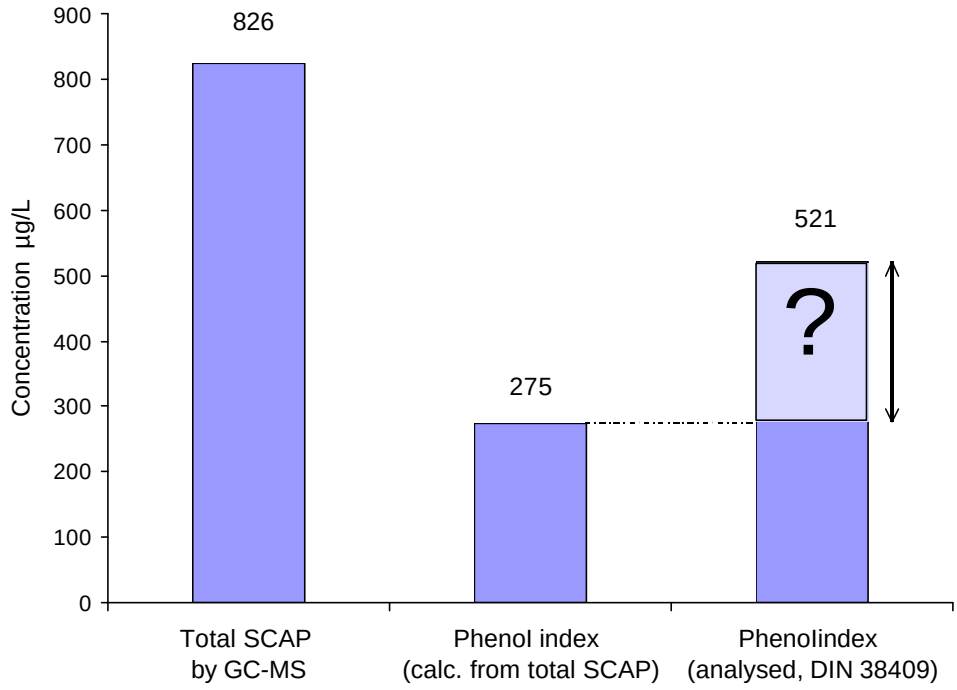


Figure 19: Total SCAP vs. *phenolindex* for well 1 (compare Tab. 12)

In sum, the *phenolindex* is not suitable for the investigation of SCAP in environmental samples, but can still provide some idea on the presence of a characteristic contamination. It is far too imprecise as an input parameter for modelling and on its basis it is rather impossible to predict the extent of contamination plumes.

4.2 HPLC

The application of HPLC in reversed phase mode was tested in the process of establishing an economic and fully automated analytical method for the investigation of SCAP as individual compounds in aqueous and solid environmental samples. Although it has been established, that the separation of all SCAP in complex matrices by HPLC is rather difficult (Lüders (1999)), an especially developed phenol column has been tested for its separation capacity for 14 SCAP. Furthermore, this was done since a standardised analytical procedure exists for the analysis of SCAP with HPLC.

4.2.1 Experimental

A Dionex/Gyncotek combined LC system was used. This system comprises an autosampler (AS50) with auto dilution and injection valve, a low pressure gradient quaternary pump with integrated degaser (P580, LPG) and a diode array detector (UV-340D). The analytical column (Ultrasep ES-Phenole 5MY, 250*3 mm i.D.) was supplied by Sepserv.

The eluents applied were acetonitrile (Baker, gradient grade), water (18 MΩ, 4 µg/L TOC) and phosphoric acid (85%, for electrochemical detectors, Fisher). Water and phosphoric acid were mixed to yield the required pH in the dilute phosphoric acid eluent. The phenol standard was purchased from Dr Ehrendorfer as Phenol Mix 1, containing 50 ng/µL of each compound (phenol, 3 cresols, 6 dimethylphenols and 4 trimethylphenols).

4.2.2 Results and discussion

The observed separations for 14 SCAP are summarised in Figure 20. In order to widen the polarity range of SCAP, the eluent is made acidic. As can be seen, the best separation is observed when the phosphoric acid has a pH of 2.5 and the acetonitrile gradient is slowly increased from 26% to 32% within 60 minutes. However, no separation was achieved for m- and p-cresol. The separation of 2.3-, 2.4- and 2.5-dimethylphenol remains difficult. Field samples may contain more than the 14 SCAP tested. This leads to even more co-eluting peaks, such as 4-ethylphenol co-elutes with 2.5-dimethylphenol and 3-ethylphenol or 3-isopropylphenol co-elutes with 3.4.5-trimethylphenol.

4.2.3 Implications

Due to the rather unselective determination of analytes by DAD the individual SCAP can not be identified by their spectra alone. Indications are retention time and phenolic spectra. For this reason, co-eluting compounds cannot be quantified. Their absence or presence as individual compounds can further not be identified since it is not possible to state which compound(s) the peak comprises. The chromatograms in Figure 20 only show standards (SCAP in de-ionised water). The analysis time of 2 hours is rather long.

In summary, it can be stated that the application of HPLC to the analysis of SCAP in real samples with complex matrices is not the method of choice. In this study the application of an especially developed analytical column could not be shown to be successful for the separation problem.

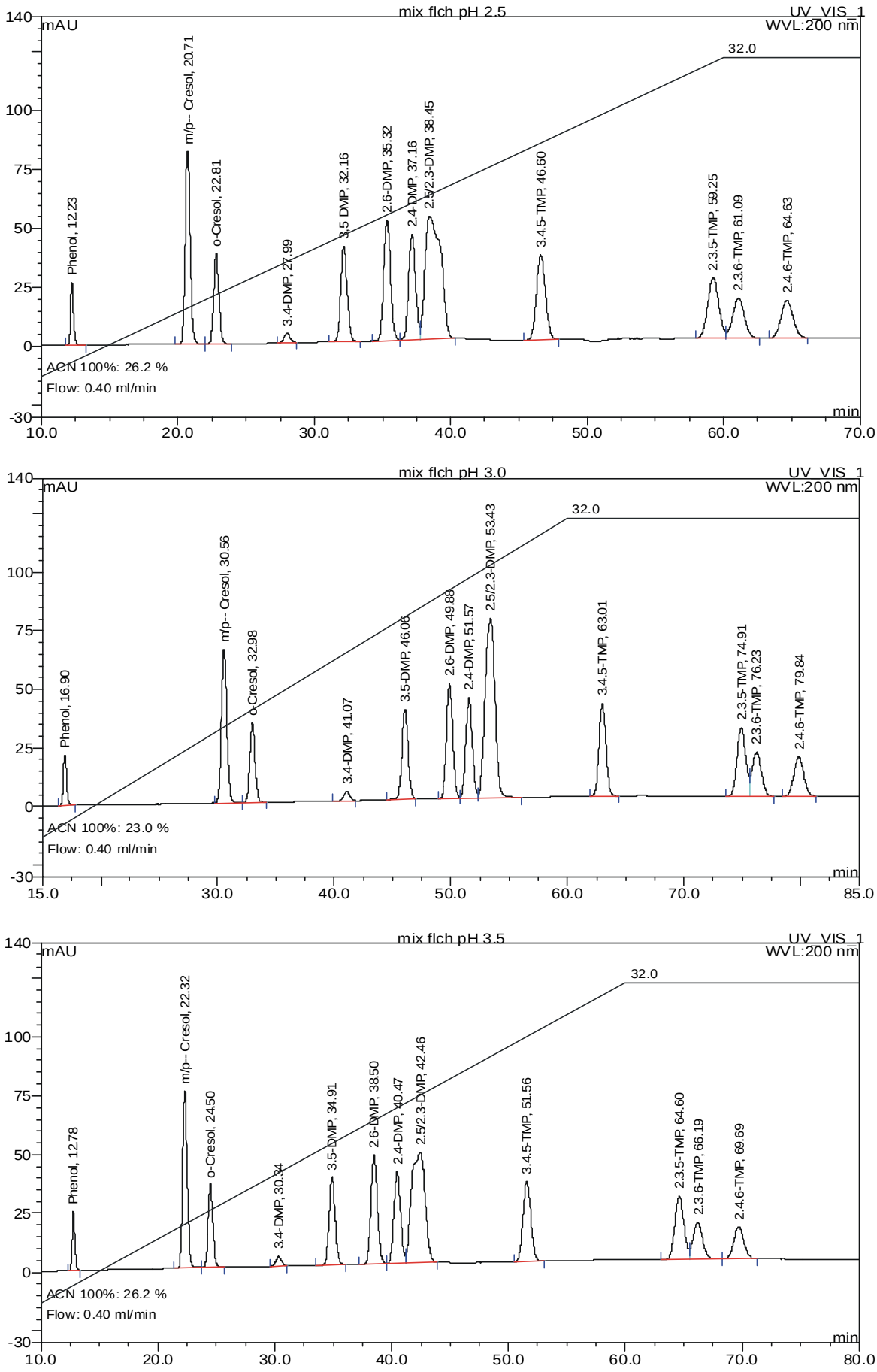


Figure 20: HPLC-Chromatograms of 14 SCAP at 3 pH values

4.3 GCMS

In order to investigate and economically monitor contamination plumes the development of a precise, robust and cost effective analytical procedure is required. Currently, there are medium polarity capillary columns available for the analysis of phenols by gas chromatography. Those are especially designed for the separation of the EPA priority phenols (EPA 604) such as phenol, cresols, chlorophenols and nitrophenols without derivatisation. However, German (DIN 38409-F15) and European standards (EN 12673) for the analysis of some chlorophenols require their derivatisation with acetic acid followed by extraction into hexane as necessary sampling preparation steps. The nearly full separation of **all SCAP without derivatisation** by GCMS has not yet been described. This direct method has been proven by own investigations to fail on standard columns as well as on columns especially designed for EPA-phenols. The newly developed method for the analysis of all SCAP without derivatisation is described below.

4.3.1 Experimental

Standards

Phenol standards were purchased from Dr Ehrendorfer as Phenol Mix 1, containing 50ng/µL of each compound (phenol, 3 cresols, 6 dimethylphenols and 4 trimethylphenols). The 3 ethylphenols and 5 propylphenols were purchased from Acros, Aldrich and Merck, respectively. The internal standard d^3-2,4-dimethylphenol was supplied by Promochem.

GCMS and capillary column

A Hewlett Packard GCMS instrument (GC: 6890, MSD: HP5972A) was used in combination with a Combi-PAL auto sampler (CTC Analytics). The separation was performed on an enantioselective capillary column (α-DEX 120, 60 m × 0.25 mm I.D., 0.25 µm film thickness) supplied by SUPELCO. It contains 20% permethyl-α-cyclodextrin dissolved in a medium polarity siloxan phase (Poly 35%phenyl/65%methyl siloxan). Carrier gas 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 than increased at a rate of 7°C/min to 136°C. After an isothermal period of 2 minutes a very slow 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, which was finally held for 7 minutes ensured the cleanup of the column. Consequently, one analysis requires 60 minutes in total. By applying the SIM mode a very good signal to noise ratio was observed. The following ions were monitored: 65, 66, 77, 90, 91, 94, 107, 108, 110, 121, 122, 125, 134, 135, 136 (m/z) with a dwell time of 100 ns each.

Headspace-Solid phase micro extraction (HS-SPME)

A polyacrylate fibre (85 µm film thickness) supplied by SUPELCO was used for the automated selective enrichment of phenols from headspace. Prior to their application to real samples, the fibres were conditioned at 300°C for 2 hours. Blank analysis confirmed the quality of conditioning.

The sample was prepared by placing an aliquot of 10 mL in a 21.5 mL headspace vial containing 2.5 g of $NaSO_4$. This mixture was spiked with 5 µL internal standard (d3-2.4-dimethylphenol). The addition of 5 drops of H_2SO_4 (96% p. A.) should enhance the phenol transfer from solution into headspace. The vials were immediately sealed and placed into the auto sampler rack (Combi-PAL, CTC). Prior to the extraction step each vial was automatically agitated at 50°C for 10 minutes. The HS-SPME was then carried out at 50°C for 45 minutes. Finally, the analytes were thermally desorbed in the split/splitless injector port of the GC at 280°C for 3 minutes with a splitless time of 60 s. A special SPME-liner (0.75 mm) purchased from Agilent improved the chromatographic performance.

SPE

The solid phase extraction was performed on a VACMASTER® system (IST) similar to the one illustrated in Figure 10 (p.4). Hydroxylated polystyrene-divinylbenzene filled cartridges (ISOLUTE ENV+,IST, 200 mg, 6mL) were used for the extraction and enrichment of SCAP. This phase has previously been described to be suitable for the quantitative extraction of priority phenols from environmental samples (RODRIGUEZ & CELA (1997)). To minimise clogging of the extraction cartridge by particles a guard cartridge was placed on top of the extraction cartridge. The guard cartridge (ISOLUTE depth filter reservoir, IST. 70 mL) contains a non absorptive sponge filter of about 3cm. After the manifold was assembled, the two cartridges were washed with 35 mL methanol (HPLC-grade). The system was then conditioned with 300 mL HCl-acidified water (pH=2) at a flow rate of 10 mL/min. Immediately after, the sample was applied at the same flow rate. Then the matrix was removed from the cartridges by applying 300 mL of HCl-acidified water (pH=2) at a flow rate of 15 mL/min. The cartridge was allowed to dry in a nitrogen stream for 20min to minimise water carry-over. Finally, the analytes were eluted from the extraction cartridge with 3 mL of methanol into a sample vial. For further concentration, the sample was reduced in volume to 1 mL in a nitrogen stream at room temperature.

4.3.2 Method description for aqueous samples

As apparent from the chromatogram in Figure 21 the inclusion mechanism that exists in permethyl-cyclodextrin columns shows an excellent selectivity for the structural isomers of SCAP. Separation was further enhanced when the cyclodextrin is dissolved in a medium polarity siloxan phase. The achieved separation of underivatised SCAP on the selected

column is comparable to reported separations of their derivatives on standard capillary columns (ROLFES & ANDERSSON (2001)).

Nevertheless, there are also drawbacks of such stationary phases. Inclusion dominated chiral separations have lower analyte capacity due to fewer interaction sites. Both, moisture and oxygen affect the selectivity and stability of these phases, therefore, good drying and oxygen traps are essential for continued optimum performance. This requires that the samples must not contain traces of water or oxygen when injected into the GC port. Last, but not least, these columns have a very limited temperature operating range which should not be more than 220°C for most applications. Additionally, the heating rate or cooling down rate should not be more than 10°C/min. Otherwise the stationary phase will deteriorate into little droplets.

These drawbacks limit the choice of applicable sample preparation techniques. LLE was primarily excluded from the list since large amounts of toxic, high purity solvents are required for this extraction process. This procedure would make the whole analytical method neither economic nor satisfy the requirements to be fast.

The application of SPE to the preparation of environmental aqueous samples followed by the analysis on a described column was examined. Although, good recovery rates (80-102%) were achieved, it was extremely difficult to fully eliminate water traces from the SCAP analytes on the cartridge. After cartridge drying in an nitrogen stream for 30 minutes and elution with methanol the extract still contained too much water as a rapidly deteriorating column (50 samples) indicated i.e. very broad peaks were observed. The chromatograms became no longer interpretable.

A simple method, which can satisfy the requirements to be fast and economical, is SPME from headspace. It keeps the introduction of water vapour onto the column to a minimum and has further advantages. The limited capacity of a SPME fibre is in good agreement with the low analyte capacity of the analytical column. The extraction from headspace yields more reliable results, increases the life time of the fibre, capillary column and mass selective detector and enables an economical application of this combined technique to a wide variety of samples. The lifetime of the column could be extended from 50 samples, when SPE is used to more than 3000 samples. HS-SPME was shown to be a suitable technique for the water free selective SCAP enrichment.

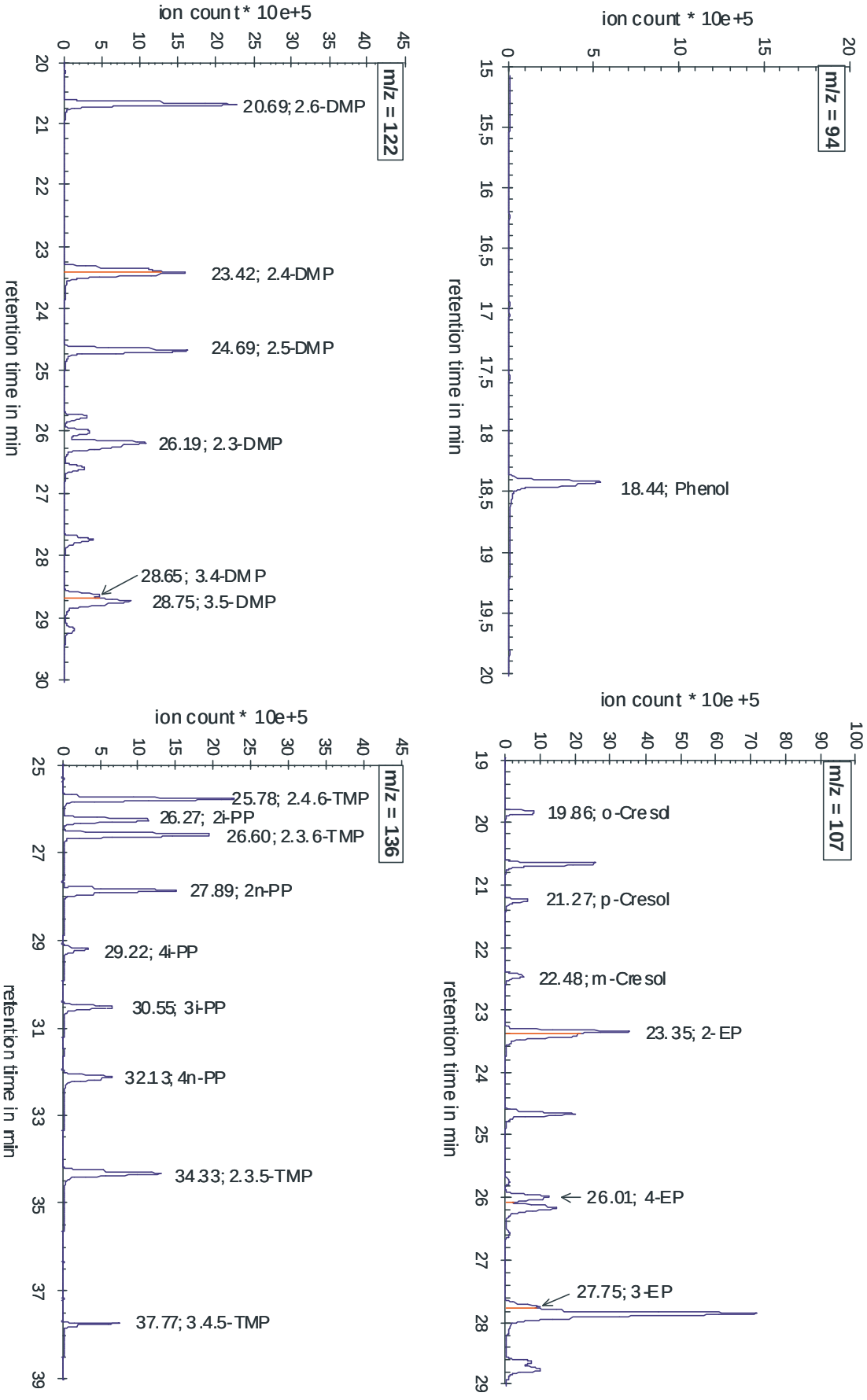


Figure 21: GC-MS chromatogram of 22 individual SCAP in tar matrix

However, the enrichment of SCAP from headspace seems rather unorthodox due to their high solubility in water. The addition of salt (250 g/L of Na_2SO_4) and H_2SO_4 (pH should be below 2) minimise the solubility of SCAP in water and support the enrichment of SCAP in the headspace. Nevertheless, the amounts of SCAP extracted from each sample is rather small compared to volatile compound extractions such as TCE or PCE. In total, between 0.15 and 1.5% SCAP are extracted by this technique (Tab. 13). On this account, sample vials can twice be analysed and still yield the same result.

Tab. 13: Proportion of SCAP in % which are removed from solution during headspace

SCAP	%	SCAP	%
phenol	0.15	2.3-dimethylphenol	0.51
o-cresol	0.32	3.4-dimethylphenol	0.40
p-cresol	0.16	3.5-dimethylphenol	0.43
m-cresol	0.21	2.4.6-trimethylphenol	1.55
2.6-dimethylphenol	0.76	2.3.6-trimethylphenol	1.25
2.4-dimethylphenol	0.78	2.3.5-trimethylphenol	0.97
2.5-dimethylphenol	0.72	3.4.5-trimethylphenol	0.34

The main parameters have been selected to demonstrate the influence of parameter variation on the extraction efficiency of SCAP from headspace with a 85 µm PA-fibre. The internal standard d3-2.4-dimethylphenol was selected as the target analyte. As demonstrated in Figure 22, the extraction efficiency is more influenced by the extraction temperature than by the salt concentration within the sample. Therefore, salt addition is not a sensitive parameter when extraction is carried out at 50°C and pH 1. The temperature dependency is very critical on the other hand. A maximum is observed at around 50°C. This is since the adsorption equilibrium at the fibre has an inverse temperature dependency than the Henry coefficient of the SCAP (also compare Tab. 2, p.8).

The pH dependency, as shown in Figure 23, shows an increased extraction efficiency for SCAP at pH values generally lower than 2. At values lower than 2, the pH dependency of the extraction efficiency becomes insensitive.

The extraction time, as shown in Figure 24, shows an increase in extraction efficiency for SCAP with time. A significant increase is observed up an extraction period of 50 min. This slow adsorption kinetic may be assigned to the solid nature of the polyacrylate film (BARTAK & CAP (1997)). Equilibrium might not be fully reached within the plotted time range. An extraction time between 40 and 60 min seems sufficient when working with an internal standard to correct for the conditions.

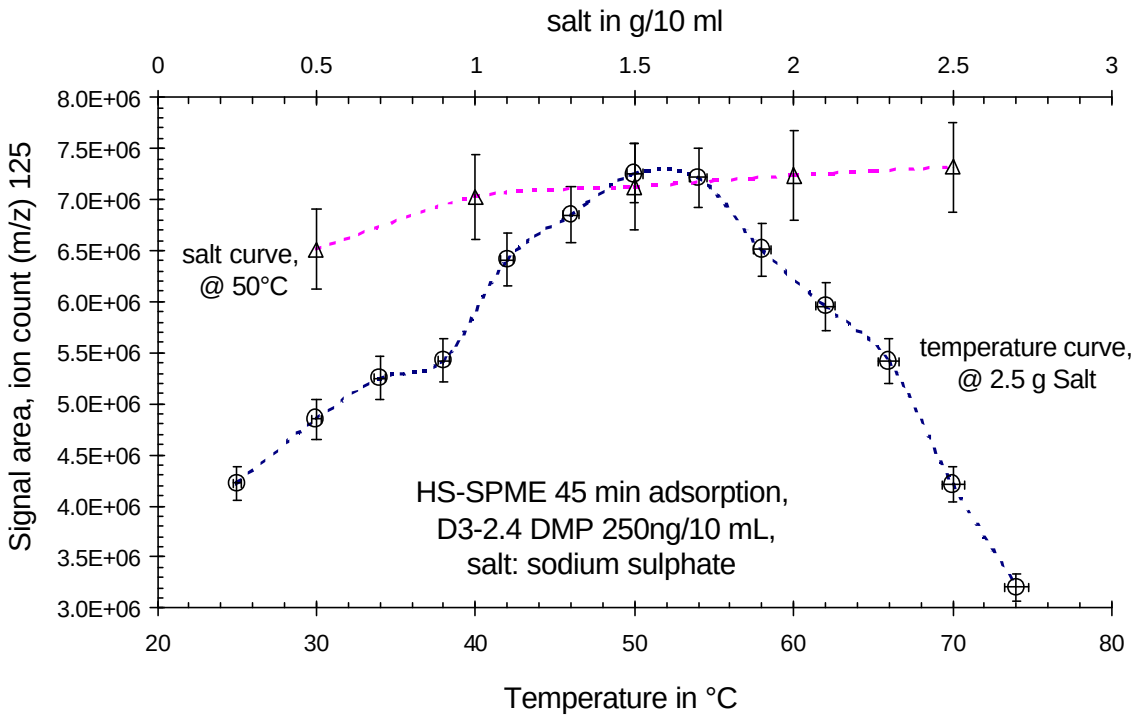


Figure 22: Temperature and ionic strength dependency of the extraction efficiency (polyacrylate fibre)

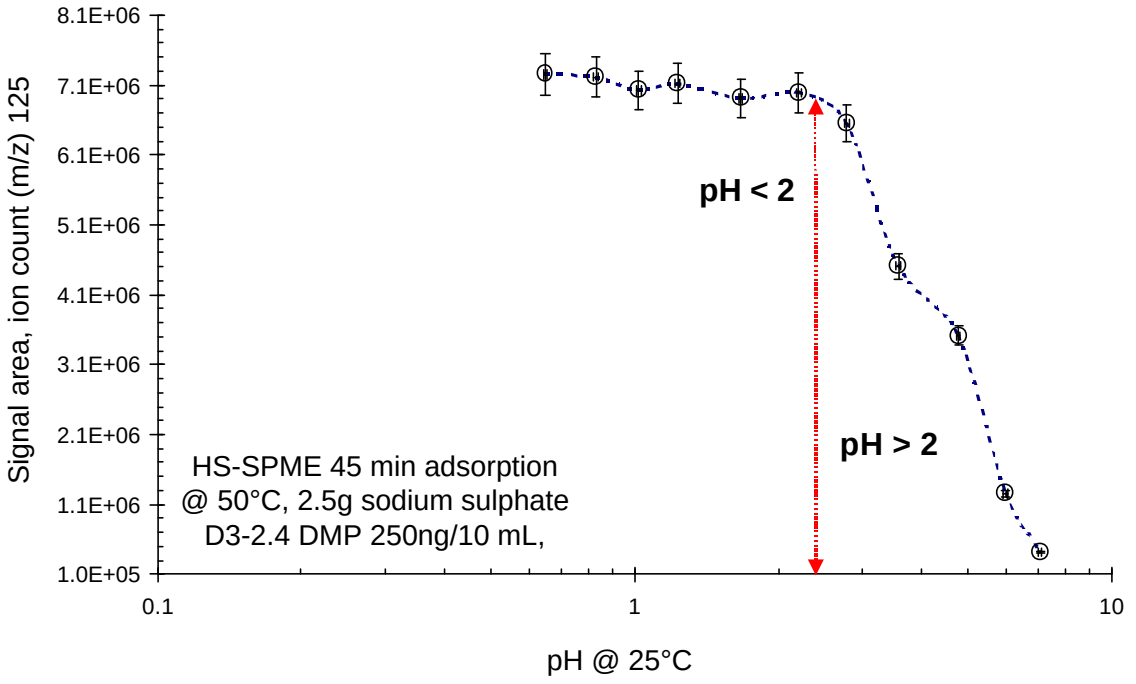


Figure 23: pH dependency of the extraction efficiency (PA-fibre)

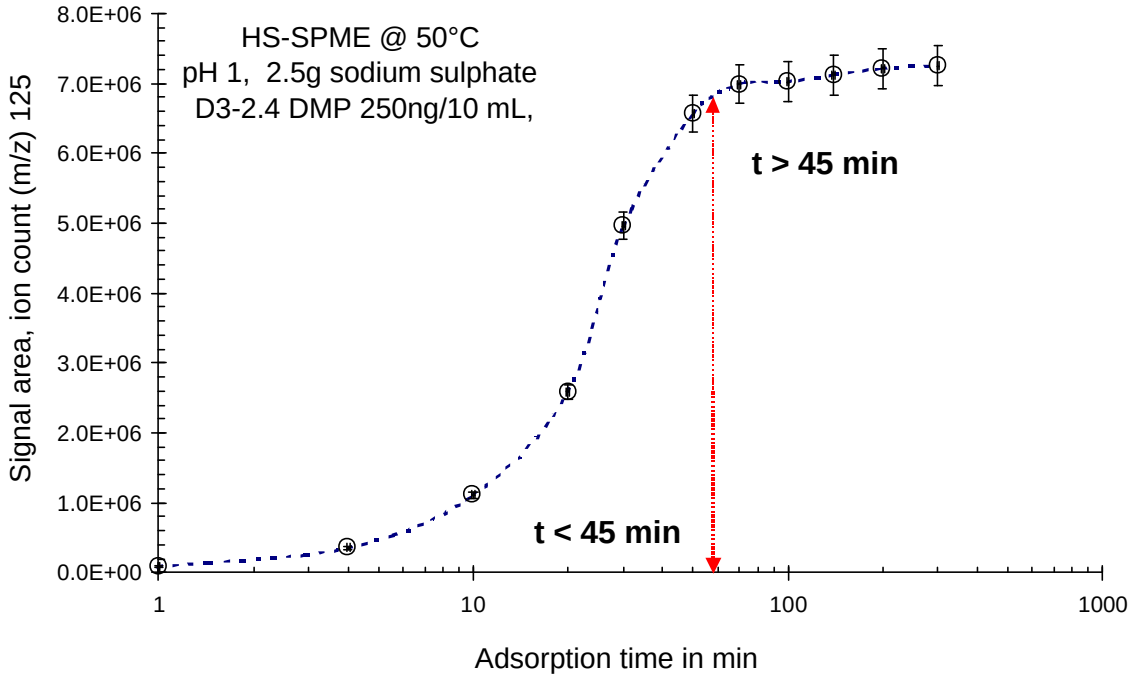


Figure 24: Extraction time vs. extraction efficiency on a PA-fibre

The lifetime of the fibre in head space mode for the analysis of SCAP by applying the parameters stated is shown in Figure 25.

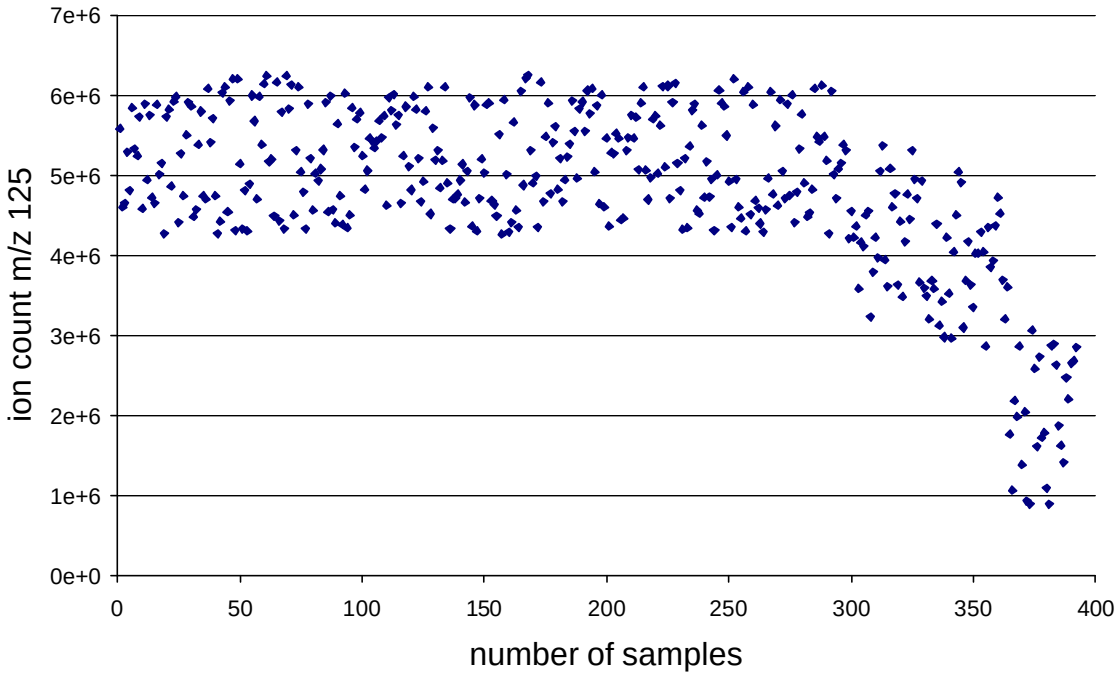


Figure 25: Fibre life time shown as the peak area of the internal standard

From Figure 25 can be seen, that the transferred mass per injection varies significantly. Therefore an analysis without internal standard is not recommended and leads to the drawbacks as described by PÖRSCHMANN *et al.* (1998), BARTAK & CAP (1997). The here applied ring deuterated internal standard 2.4-dimethylphenol was validated to be a suitable standard for all SCAP by the standard addition method. Additionally, this internal standardisation allows the use of the same calibration plot for different polyacrylate fibres of the same thickness.

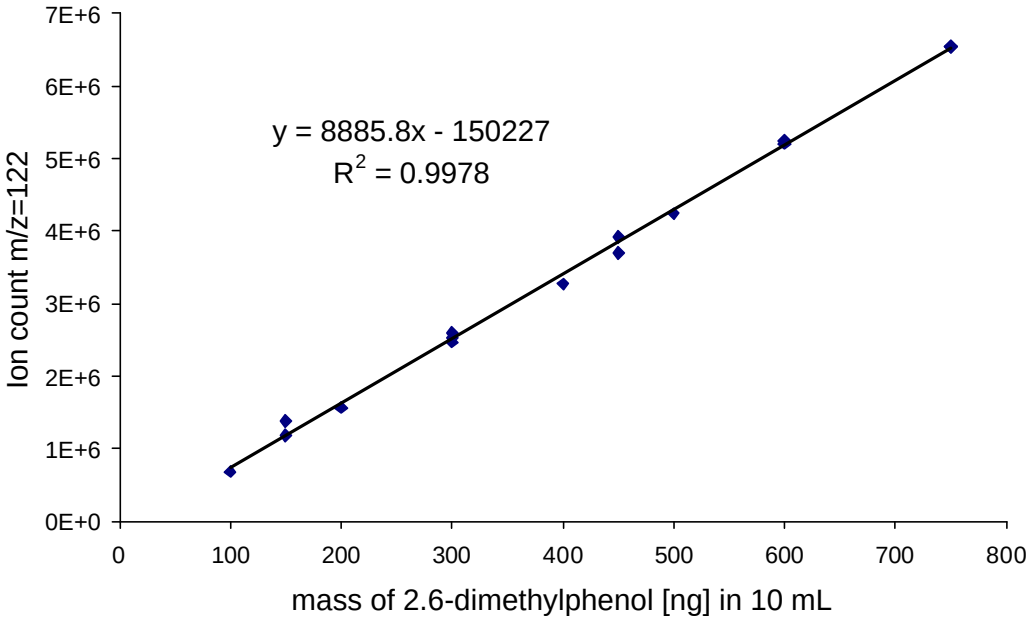


Figure 26: Combined calibration plot for 2.6-dimethylphenol observed from 4 different fibres

Figure 26 shows a combined calibration plot observed with 3 different fibres over the time interval of 5 months. This implies that the use of internal standardisation lets all calibration data for each compound plot on a single straight line.

4.3.3 Extension to solid samples

Drilling cores from mainly carbonate formations within the saturated zone were collected during this study. Those samples were generally wet and could be treated as slurries after grinding. First experiments were conducted by sampling the headspace of these slurries. This working method has frequently been described to be successful for the analysis of organics in soil samples (e.g. PAWLISZYN (1997), BACIOCCHI *et al.* (2001)). As most samples were carbonate samples (limestone, dolomite) the sample acidification was due to a CO_2 generation in a sealed headspace vial impossible.

Unfortunately, SCAP are rather soluble in water and the water content largely determines their extraction efficiency when acidification is impossible. The application of freeze drying for phenol analysis has proved to fail since samples had lost most SCAP during the drying

process. The likely approach to achieve constant extraction conditions was mixing the wet ground samples with anhydrous sodium sulphate. This however makes precise calibration very complicated due to the lack of standards. For those reasons this direct approach was no longer followed and the samples needed to be extracted. Almost all methods reported for the extraction of organic contaminants from solid samples make use of organic solvents. However, as demonstrated in Figure 27, such organic solvents are not compatible with SCAP extraction by HS-SPME as described before.

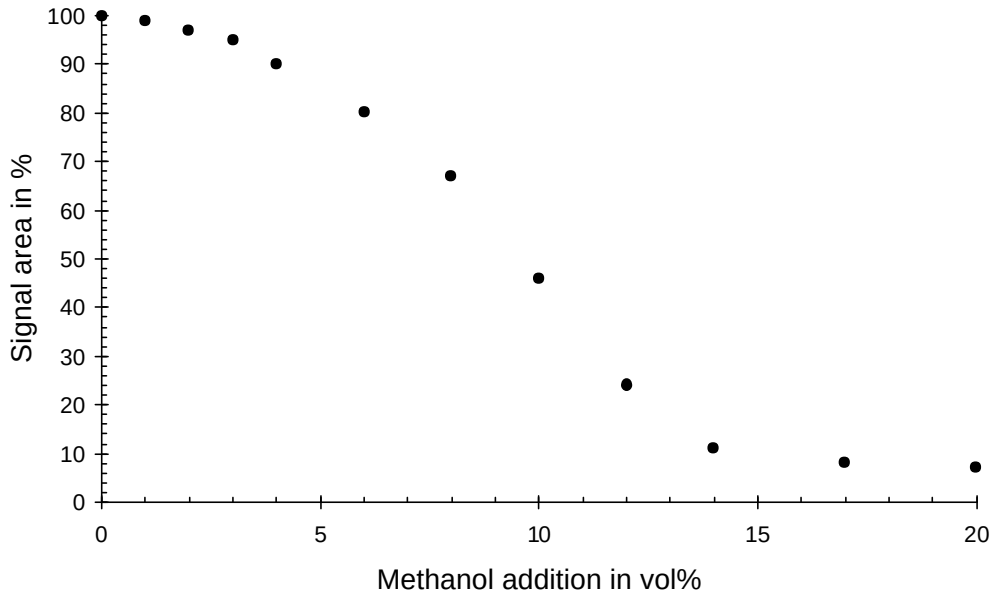


Figure 27: Average signal suppression on phenol in HS-SPME vs. methanol content in %

A significant loss of extraction efficiency is already observed in the presence of 10% methanol in the extract. This effect is mainly due to the higher solubility of SCAP in the extract, i.e. degreased tendency to be present in the headspace. Furthermore, the high methanol concentration competes with SCAP for adsorption sites on the SPME-fibre. For these reasons, an extraction method for solids (validated for dolomite) was developed which combines a high extraction efficiency with the benefits of SPME from headspace.

Experimental

Sample preparation

Two clay samples and three ground dolomite samples were vacuum freeze dried prior to extraction. The same samples were additionally weighed in “wet” and a proportion separately dried at 60°C to calculate the water content.

Soxhlet

The soxhlet extraction thimbles and glass wool were pre-extracted with 250 mL of dichloromethane - methanol (93-7) for 8 hours. The sample was homogenised and exactly 10 g weighed into a clean thimble. As an internal standard 50 µL of ring deuterated 2.4-

dimethylphenol solution (50 ng/µL) was added. Glass wool was placed on top of the sample to keep the extract solution free of particles and the system assembled for extraction. The spiked sediment was extracted with 100 mL 0.05 N NaOH for 12 hours. Boiling chips were added to the solvent to ensure the boiling process. After the extract was allowed to cool down, it was removed and stored in glass bottles at 4°C until analysis.

Microwave Assisted Extraction of Solid Samples

Approximately 25 g wet sample was added to the extraction vessels and mixed with 40 mL of 0.05 N NaOH and 50 µL of the deuterated internal standard (50 ng/µL). The vessels were heated for 55 minutes at 120°C in the microwave. After cooling down, the extract together with the solid was transferred into two 50 mL centrifuge vials and centrifuged for 15 minutes at 8000 rpm. The extract was finally transferred into a 100 mL flask and filled with distilled water to give an end volume of 100 mL. The extract was stored at 4°C until analysis, which was carried out no longer than 10 days after extraction.

Results and discussion

The freeze dried samples showed a 100 times reduced SCAP concentration as their wet weight in counterparts. This was expected, since SCAP and water are close boiling compounds in vacuum. Therefore, freeze drying of samples is not recommended.

Results from soxhlet extraction showed no observable SCAP concentration at all (i.e. recovery rates equal 0). It is suspected, that the phenols polymerised under the extraction conditions (high pH, oxygen, light and heat). This is in agreement with HAMDI *et al.* (1993), HIGASHIMURA *et al.* (2000) and PÖRSCHMANN *et al.* (1996) because a brownish to black precipitate had formed on the walls of the extraction flask. Since soxhlet extraction proofed to be a rather work intensive, energy and time consuming procedure, its optimisation for SCAP extraction from dolomite and clay was no longer continued. In order to use HS-SPME together with the benefits of the analysis of SCAP without derivatisation, an organic solvent free microwave assisted extraction method for solid samples was developed. The results for this extraction procedure showed a good recovery rate of SCAP from dolomite samples. Observed recoveries are summarised in Tab. 14. The method was easy applicable, fast and allowed the simultaneous extraction of 12 samples as desired in the process of extending the HS-SPME-GCMS to solid samples.

Tab. 14: Recovery rates for SCAP from ground dolomite samples with MAE

SCAP	%	SCAP	%
phenol	99	3.4-dimethylphenol	100
o-cresol	102	3.5-dimethylphenol	102
m-cresol	104	2.4.6-trimethylphenol	91
p-cresol	105	2.3.6-trimethylphenol	85
2-ethylphenol	92	2.3.5-trimethylphenol	95
3-ethylphenol	98	3.4.5-trimethylphenol	91
4-ethylphenol	98	2-iso-propylphenol	91
2.6-dimethylphenol	77	3-iso-propylphenol	94
2.5-dimethylphenol	97	4-iso-propylphenol	87
2.4-dimethylphenol	90	2-n-propylphenol	85
2.3-dimethylphenol	98	4-n-propylphenol	85

4.3.4 Summarising the analytical method for SCAP

The direct[17] analytical technique (HS-SPME-GCMS) allows the analysis of 24 samples per day in a fully automated process. Achievable limits of detection 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 - phenols, respectively. By using a deuterated internal standard (ring deuterated 2,4-dimethylphenol) a high reproducibility (100% +/- 5%) is achieved. The internal standard addition technique allows to evaluate the partitioning the SCAP between the aqueous phase and dissolved organic matter simultaneously (e.g. PÖRSCHMANN *et al.* (2000), DOLL *et al.* (1999)).

Tab. 15: Characteristic data for the analytical method [18]

SCAP	**Aqueous sample (µg/L)**			**Solid sample (µg/kg)**		
	Limit of detection	Limit of determination	Limit of quantification	Limit of detection	Limit of determination	Limit of quantification
Phenol	2.95	5.90	8.85	11.80	23.60	35.40
Cresols	0.21	0.42	0.63	0.84	1.68	2.52
Ethylphenols	0.35	0.70	1.05	1.40	2.80	4.20
Dimethylphenols	0.14	0.28	0.42	0.56	1.12	1.68
Trimethylphenols	0.08	0.16	0.24	0.32	0.64	0.96

The characteristic data for the developed analytical method (HS-SPME-GCMS) are

[17] direct: without derivatisation

[18] method applied: DIN 32645, blank procedure

summarised in Tab. 15. The data were determined in accordance with DIN 32645, blank procedure. The method was further verified and evaluated on real samples. The results are presented in chapter 7.

4.4 Looking back at the chapter

It is shown, that the *phenolindex* is not suitable for the investigation of SCAP in environmental samples. Most SCAP react with a decreased sensitivity and are underrepresented by the index. Paraalkyl-SCAP are not detectable by this method. Simultaneously, other contaminants such as anilines and heterocyclic compounds which almost always appear together with SCAP give a positive *phenolindex* result. Therefore it must be concluded that the sum parameter is far too imprecise for the assessment of the extent of a plume.

The separation and detection of SCAP in samples with complex matrices by HPLC methods even on specially developed columns is not recommended since some SCAP co-elute with one another or other matrix compounds. This complicates the analysis of SCAP and may lead to misinterpretations.

All previously reported procedures for the analysis of all individual SCAP compounds by GC methods require a substantial effort in sample preparation. 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 a precise, robust and cost effective analytical has been developed and evaluated on field samples. This analytical method takes advantage of the latest and commonly established developments in sample preparation and gas chromatography column technique. It could be shown that the separation of underivatised SCAP on medium polarity columns with permethyl-α-cyclodextrin added is possible. Together with headspace SPME, for the selective, water free extraction of SCAP and their selective transfer to the GC injector, the method is economic and works fully automated. It is a sensitive and selective analytical procedure which can be applied to very complex samples.

The developed analytical method has been applied to a variety of field samples. The results are presented in Chapter 7 and in the Appendix.

5 SCAP adsorption- a mechanistic approach

5.1 General introduction

Definitions

Sorption is a general term which describes the distribution process of compounds across an interface. It includes the processes of adsorption, desorption and absorption. In geosciences the term sorption is often applied to all interfaces.

Ab*sorption** takes places ***across a liquid interface and therefore involves liquid-gas and liquid-liquid interfaces. Very viscous phases are still treated as liquid, whereas sub-cooled phases must be treated as solid phases.

Ad*sorption** is the process which describes the partitioning of compounds from a gaseous or liquid phase ***onto a solid or liquid surface. This process is observed on gas-solid interfaces and solid-liquid interfaces. **Desorption** describes the reverse process of adsorption. Adsorption has traditionally been divided into two extremes: weak **physisorption** and strong **chemisorption**. Physisorption has adsorption energies typically –5...-40 kJ/mol. It is rapid and reversible. Chemisorption (specific adsorption) involves the strong bonding of the adsorbate to the adsorbent, often resulting in a change in both the surface and adsorbate chemical character. It is characterised by high adsorption energies (< -40 kJ/mol). The reactions are likely to be slow, and less readily reversible.

Isotherms describe the equilibrium relationship between bulk activity of adsorbate in solution and the amount adsorbed on the surface at constant temperature. Experimental data are usually characterised by one of the following empirical isotherms: Henry, Freundlich, Langmuir or BET.

Factors affecting adsorption

Generally, the factors affecting adsorption of organic molecules (i.e. contaminant) are surface area, surface properties, the soil organic matter (SOM) accessible at the surface and the nature of this SOM, solubility of the organic molecules (i.e. contaminant) in the liquid phase (i.e. contaminant pool or polluted water), the salinity, pH, co-solvents or DOC and finally the temperature. Since adsorption is an exothermic process, adsorption decreases with increasing **temperature**. Adsorption is directly related to the specific **surface area**. Increasing the specific surface area results in an increase in the specific

adsorption. Only compounds that tend to ionise are affected by **pH**, the only influence on neutral molecules would be the change in the character of the surface. Changes in pH will dramatically affect organic acids and bases by changing their solubility in water. Cations resulting from the protonation of an organic base, for example, may more strongly sorb to soils then their neutral species. As pH changes, surface charge also changes, and the adsorption of charged species will be affected. Neutral molecules are generally less affected by **salinity**, but often show an increased adsorption with increasing salt concentration due to the salting out (KARICKHOFF *et al.* (1979)). Increased salinity may also change the interlayer spacing of layer clays, as well as the morphology of soil organic matter.

Adsorption from solutions of non-electrolytes

Generally, aqueous solutions of organics (non-electrolytes) represent at least a two component system, i.e. aqueous phenol solutions contain phenol and water. Depending on the nature of the solid surface either the water as the solvent or the organic as the solute (i.e. phenol) is preferentially adsorbed. The resulting function is known as the surface excess isotherm (SEI). "SURFACE EXCESS OF A GIVEN COMPONENT IS DEFINED AS THE DIFFERENCE BETWEEN THE AMOUNT OF COMPONENT ACTUALLY PRESENT IN THE SYSTEM AND THAT WHICH WOULD BE PRESENT (IN A REFERENCE SYSTEM) IF THE BULK CONCENTRATION IN THE ADJOINING PHASES WERE MAINTAINED UP TO A CHOSEN GEOMETRICAL DIVIDING SURFACE." (IUPAC). In other words, surface excess represents the adsorbed amount of a given component relative to its concentration in the liquid phase, i.e. the higher the solubility of a compound in the liquid phase the less it is adsorbed.

For dilute solutions the adsorption isotherm for the solute is usually of interest and is therefore recorded. This isotherm lays in the first quadrant of the coordinate system when the concentration of the solute in solution is plotted against the surface excess in equilibrium. If water is preferentially adsorbed, the isotherm for the solute is negative and is found in the fourth quadrant. This is because the solution gets more concentrated when it is reduced in its water content.

Beside a preferential adsorption, this solvent solute competition is important in groundwater aquifer interaction. Many aquifer materials are silicates or oxides. These surfaces possess hydroxyl sites which strongly attract water, creating a layer of tightly-bound water at the surface. Thus, the adsorbing organic molecule "sees" a layer of water and any direct association with the aquifer surface must first displace that water. This correlation is shown on substituted phenols by EVANKO & DZOMBAK (1998). When hydrophobic molecules associate with soil organic matter, however, there is no competition with water. This difference may complicate interpretations for phenolic

groundwater contaminations when laws derived from insoluble organic contaminants are straight forwardly applied to these contaminants.

Relevance of adsorption in aquifer systems

Surfaces capable of adsorbing ions and compounds are ubiquitous and therefore adsorption is an attenuation mechanism that can be present in virtually any groundwater system. Adsorption to immobile sediments is the basic concept of retardation, and as such is fundamental to an understanding of contaminant transport. Adsorption to mobile sediments can also be of critical importance.

Current knowledge suggests that adsorbed compounds are no longer available to micro-organisms. Certain surfaces such as manganese III/IV oxids (STONE & MORGAN (1984A), STONE & MORGAN (1984B), STONE *et al.* (1987)) can however accelerate abiotic and biotic transformation reactions, such as hydrolysis and redox. Adsorption can both; mobilise and immobilise a dissolved contaminant, enhance and inhibit contaminant degradation.

Frequently employed empirical isotherms

Freundlich: A frequently employed empirical isotherm is the Freundlich relationship, which is often applied to describe the adsorption processes seen in natural systems.

This relationship is expressed by the following equation:

$$C_s = K_{Fr} \cdot C_w^n \qquad [1]$$

c_S: equilibrium concentration on solid,
cw: equilibrium concentration in liquid,
K: partitioning constant,
n: Freundlich exponent

For organic solutes n is often found to be slightly greater than 1. Ambiguities originating from the concentration dependent nature of the Freundlich coefficient are discussed by Carmo *et al.* (CARMO *et al.* (2000)). URANO *et al.* (1981) and MANES (1998) suggested an unit-equivalent Freundlich coefficient by normalising C_w to the water solubility of the compound:

$$C_s = K_{Fr}^* \left(\frac{C_W}{S} \right)^{1/n} \qquad [2]$$

where S and K_{Fr}^* denote the water solubility [mg L^{-1}] of the compound, and the unit-equivalent Freundlich coefficient [mg kg^{-1}], which can be calculated by $K_{Fr}^* = K_{Fr} S^{1/n}$.

Langmuir Type: This isotherm mainly represents chemisorption. Adsorbing molecules sequentially fill surface sites until a mono-layer coverage is achieved. However, no multi-layer coverage is included. Each site is equivalent in energy. Langmuir behaviour assumes fast reversible adsorption, and interaction only between adsorbate molecules and the surface site. The equation for the Langmuir isotherm is usually given as:

$$c_s = \frac{a\ \Gamma_{max}\ c_L}{1 + a\ c_L} \qquad [3]$$

c_S: equilibrium concentration on solid,
c_L: equilibrium concentration in liquid,
α: adsorption constant,
Γ_{max}: maximum amount adsorbed in a mono-layer

While the Langmuir isotherm is rarely useful in real, heterogeneous systems, it illustrates the concept of a mono-layer coverage rather well.

Langmuir-Freundlich Equation:

This combined isotherm has been proposed by DABROWSKI (1986) to analytically describe S-shaped isotherms. So far, this approach has been used to describe the adsorption isotherms for non-ideal mixtures on heterogeneous surfaces.

BET Type: The BET equation accounts for a multi-layer coverage and is often applied to gas adsorption on solids. Main application of this isotherm type is in determination of the specific surface area of solids with nitrogen at its boiling point (77.35K). At high pressures P, the adsorbate condenses to a bulk liquid on the surface, the number of layers becomes infinite. This isotherm describes well the physisorption of an organic vapour onto very dry surface soils.

$$c_S = \frac{\Gamma_{max}\ K\ p}{\left(p^0 - p\right)\left[1 + \left(K - 1\right)\left(\frac{p}{p^0}\right)\right]} \qquad [4]$$

c_S: equilibrium concentration on solid,
Γ_{max}: maximum adsorbed amount.,
K: adsorption constant related to enthalpy of adsorption,
p: partial pressure,
p^0: saturated vapour pressure

While this is effective in describing vapour-phase adsorption on dry soils, it does not describe electrostatic interactions of ions onto a heterogeneous surface in an aqueous system.

Mechanistical approaches to adsorption

The adsorption literature has reported numerous adsorption isotherms, measured for many different adsorbents and adsorptives. A general classification of adsorption isotherms from solution onto solids was made by OSTWALD & DE IZAGUIRRE (1922). They describe various curves, having maxima in adsorption from binary solutions in molar fraction ratios. BRUNAUER *et al.* (1938) later defined five types of vapour-phase adsorption isotherms. A widely accepted and applied classification of solute adsorption isotherms is

given by GILES *et al.* (1974A). These concepts (Tab. 16) where mainly drawn from earlier mechanistic orientated studies (GILES *et al.* (1960)). Isotherms for adsorption of organic solutes are divided into four main classes, according to the nature of slope of the initial portion of the curve, and thereafter into sub-groups. The main classes are: (a) *S* Curves, indicative of vertical orientation of adsorbed molecules at the surface. (b) *L* Curves, the normal or "Langmuir" isotherms, usually indicative of molecules adsorbed flat on the surface, or, sometimes, of vertically oriented adsorbed ions with particularly strong intermolecular attraction. (c) *H* Curves ("high affinity") (commencing at a positive value on the "concentration in solid" axis), often given by solutes adsorbed as ionic micelles, and by high-affinity ions exchanging with low-affinity ions. (d) *C* Curves ("constant partition"), linear curves, given by solutes which penetrate into the solid more readily than does the solvent. Thus, if the adsorbed solute molecules in the mono-layer are so oriented that the new surface they present to the solution has low attraction for more solute molecules, the curve has a long plateau; if they are oriented so that the new surface has high attraction for more solute, the curve rises steadily and has no plateau.

Tab. 16: General Isotherm classification according to GILES *et al.* (1960)

Type	Interpretation	Conditions required	Example
S	adsorption becomes easier as concentration rises	- solute molecule is monofunctional - solute molecule has moderate intermolecular attraction - strong competition for substrate sites	phenol on alumina from water
L	the more sites are filled the more difficult to find vacant sites	- adsorbed solute is not vertically oriented - no strong competition from solvent	phenol on alumina from benzene
H	special case of L-curve, where in dilute solutions solvent is completely adsorbed	- as in L, often species are adsorbed in large units i.e. micells	chemisorption of fatty acids on Raney Nickel
C	linear distribution till a plateau occurs due to site all occupied	- porous substrate with flexible molecules - regions of differing degrees of crystallinity - higher affinity for substrate than solvent - better penetration power	PAH on NOM

The theoretical concepts as shown in Tab. 16 where testified by a number of experiments GILES *et al.* (1974B).

Experimental methods for investigating adsorption

Generally one can divide the experimental methods to investigate the adsorption behaviour into **dynamic experiments** and **static experiments**.

Dynamic experiments are very common in investigating the adsorption behaviour of materials which are exposed to a flow of adsorptive, i.e. materials in adsorber columns and aquifer material or even liquid chromatography. The dynamic method is often also referred to as column experiment. The experimental design contains a column, which is filled with water saturated adsorber material. A pump or hydraulic potential creates a flow across the column with the inflow set at the bottom. In those studies it is vital to know the hydraulic properties which is usually assured by applying a conservative tracer. The boundary and starting conditions in column studies help to simulate the adsorption property and adsorption capacity under various flow conditions and to forecast the behaviour of real systems. It can also provide some idea on the transport controlled adsorption kinetics. The shape of the resulting breakthrough curves provide only little information on the adsorption mechanism.

Static experiments, also referred to as batch experiments, are done under controlled and partition equilibrium conditions. Therefore such experiments allow the investigation of the adsorption mechanism. The experimental design varies with the aim of the experiment, i.e. the investigation of a diffusion controlled adsorption mechanism starts with solvent equilibrated adsorbent to which the adsorptive is added and the batch is left standing without shaking until eventually the adsorption equilibrium is reached. If diffusion and displacement of adsorbed water as limiting factors should be cancelled out the (dilute) solution of adsorptive is added to the dry adsorbent. Regularly shaking of the sample should force the reaction and thus decrease the time needed to reach equilibrium.

5.2 Previous research on phenol adsorption

Adsorption processes of phenol and its derivatives from aqueous solutions were extensively studied under technological aspects such as production processes and the purification of industrial waste-waters or drinking water (BANAT *et al.* (2000), BERCIC & PINTAR (1996), BINIAK *et al.* (1990), CEYHAN *et al.* (1999), HAGHSERESHT & LU (1998), QADEER & REHAN (2002), WOLFF *et al.* (1986)). Adsorption of SCAP on activated carbon is in the above cited papers mainly described by Freundlich or Langmuir isotherms. A comprehensive compilation of the adsorption behaviour of various phenols from several solvents onto different adsorbates is presented in a paper from GILES *et al.* (1960) and summarised in Tab. 17.

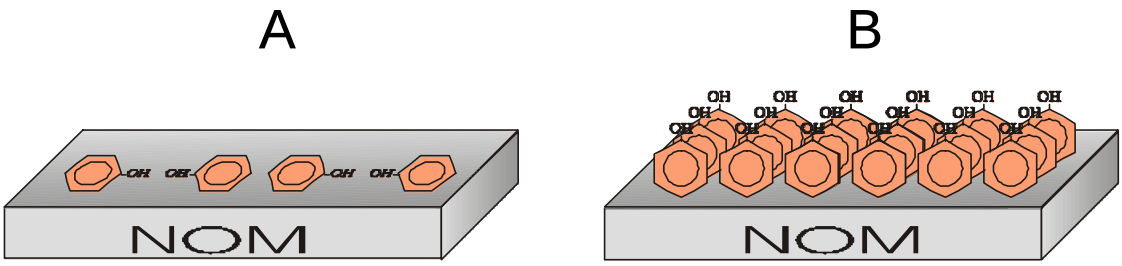
Tab. 17: Adsorption Isotherms for phenolics according to GILES *et al.* (1960)

Adsorptive	Solvent	Adsorbate	Type
m-, *p*-Nitrophenol	H_2O	Silk	*S*1
2,4-Dinitrophenol	H_2O	Al_2O_3 (anodic film)	*S*1
Phenol	H_2O	Nylon	*S*1(?)
Phenol	H_2O, Ethanol	Wool	*S*1
Phenol, *p*-cresol, *m*- and *p*-fluorophenol	H_2O	polyglycine	*S*1(?)
Monosubstituted Phenol:	H_2O	Wool	*S*1
p-Nitrophenol	H_2O	SiO_2	*S*2
Phenol	H_2O	Al_2O_3	*S*2
Phenol	H_2O, iso-Octanol	Charcol	*S*2
Phenol	H_2O	anthra quinonene derivative pigment	*L*2
Phenol	H_2O	charcol	*L*2
p-Nitrophenol	C_6H_6	Al_2O_3	*L*3
Phenol	iso-Octanol	wool	*L*3
Phenol	H_2O	graphite	*L*5
p-Nitrophenol	H_2O	graphite	H*5* (?)
p-Nitrophenol	C_6H_6	nylon	*C*1
p-Nitrophenol, *p*-bromophenol	H_2O	polyglycine	*C*1
Phenol	H_2O	cellulose triacetate	*C*1
Phenol	iso-Octanol	cellulose triacetate	*C*1
Phenol	H_2O	silk	*C*1 (?)
Phenol	H_2O	Terylen polyester	*C*1
Phenol, *p*-cresol, and monohal.-phenols	H_2O	Polyphenylalanine	*C*1

A sophisticated mechanistic interpretation of experimental isotherms requires fundamental knowledge on the specific interaction of phenol molecules with the adsorbent surface. GILES *et al.* (1960) (Tab. 17) observed a s-shaped isotherm for phenol from its aqueous solution onto graphite. They assigned the S-Type isotherm to multimolecular adsorption effects. This isotherm has a very similar shape as the Brunauer type II has which itself had been reported for gas adsorption onto nonporous solids and is also interpreted to be caused by multimolecular adsorption effects (BRUNAUER *et al.* (1938)). URANO *et al.* (1981) studied the adsorption isotherms for 16 organic compounds including phenol on activated carbons and used a modified Freundlich isotherm for plotting the adsorbed amounts of phenol against the reduced subsequent aqueous concentration. This approach draws a clearer picture for very soluble compounds when their surface excess isotherms are compared.

From the descriptions of GILES *et al.* (1960) the following phenol orientation is suggested in the system: water- natural organic matter (NOM) (Figure 28). A detailed introduction to

this change in orientation is provided for 3,4-dimethylphenol later in this chapter.



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

Molecular orientation at high phenol concentration (well beyond 1000 µg/L)

Figure 28: Orientation of phenol molecules from their aqueous solution onto natural organic matter (NOM)

Distribution coefficients of phenolic solutes between water and polar or non-polar organic solvents are given in ABRAMS & PRAUSNITZ (1975) and WON & PRAUSNITZ (1975). Investigations on the adsorption of phenol from multicomponent systems has been described by FLEIG (1995) and HALHOULI *et al.* (1997). The adsorption capacity of the quaternary sediments in the area Deuben was investigated by BLUHM-JANßEN (1998). She describes a very low adsorption capacity for those sediments.

SEIDEL *et al.* (1985) measured the adsorption isotherms of phenol and indol on activated carbons. In contrast to the general temperature dependency of adsorption, it was observed that at higher temperature more phenol is adsorbed. The competitive adsorption of phenol and indol on activated carbon from aqueous solutions has been reported ANTONJUK *et al.* (1991). GELBIN *et al.* (1982) investigated the phenol adsorption properties in relation to the structure of the activated carbon (i.e. containing partially micro porous structures) by measuring breakthrough curves of phenol. For the short-time adsorption the authors used a diffusion coefficient of $D = 33\ 10^{-10}$ cm^2/s and for the long time range a diffusion coefficient of $3.4\ 10^{-10}$ cm^2/s.

5.3 Characterising the adsorbents

In order to investigate the adsorption mechanism in greater detail, the adsorbents must be characterised in terms of their surface properties.

5.3.1 Subbituminous coal

This type of coal was chosen as a model adsorbent since this is the predominant coal type of the seams present in the field areas described in chapter 7. The coal samples were derived from seam 1 of the open cast mine “Profen Süd”. The analysis for sulphur

and TOC yielded 55% TOC and 1.2% sulphur, which confirmed its classification as subbituminous coal. Subbituminous coals are thermally altered residues of developed plants that remain after exposure to higher temperatures and pressure (40 - 100 °C). It should be emphasised that coals and kerogen are heterogeneous by definition (VAN KREVELEN (1993)), consisting of a variety of different components (macerals). Coals are composites consisting of a macromolecular three-dimensional network of condensed aromatics (polymers) and separate molecular compounds (not polymeric), with only the latter being typically soluble in organic solvents (aliphatic, aromatic hydrocarbons and heterocyclic compounds).

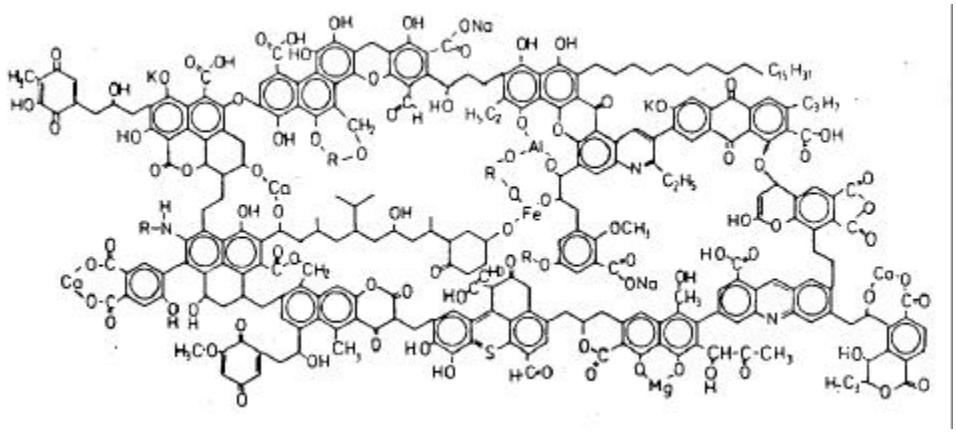


Figure 29: Molecular structure of subbituminous coal[19]

The adsorption of phenol from aqueous solution for determining the surface area was suggested in KIPLING (1965). A single curve is observed if adsorption per unit area is plotted for three carbon blacks of different surface characteristics. A multi-layer approach however, was not investigated. An attempt was made by BOEHM & GROMES (1959) to apply the modified BET equation to the adsorption of phenol. With carbon tetrachloride as the solvent and clays and silica gels as the adsorbents, this gives “mono-layer values” from which specific surface areas were calculated in close agreement with those obtained from low-temperature adsorption of nitrogen. In an extended study on porous carbons NAUCKE (1963) showed that the ratio of the specific surface areas determined from adsorption of phenol and of nitrogen or argon widely varied between samples. Interpretations are based on mole sieve effects and multi-layer surface coverage.

[19] in: HÜTTINGER & MICHENFELDER (1987)

Nitrogen adsorption isotherm

The coal sample was degassed at 180 °C for 24 h. Nitrogen adsorption isotherms were derived at 77.1 K (-196°C, boiling point of N_2) on an ASAP 2010 (Micromeritics). The resulting plot is shown in Figure 30. The isotherm is a little concave to the p/p° axis, then almost linear and finally convex to the p/p° axis. It indicates the formation of an adsorbed layer whose thickness increases progressively with increasing relative pressure until p/p°? 1. This indicates a non-porous or macroporous adsorbent. No micro or meso pores were detected. This may be due to a blockage of the pores by highly viscous organic compounds, present in subbituminous coals.

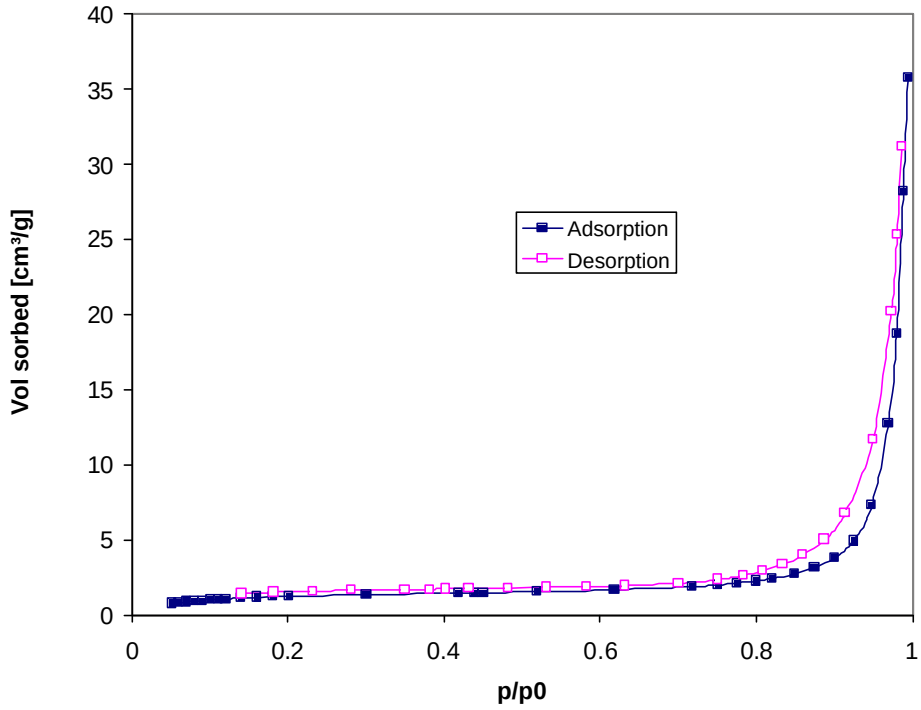


Figure 30: N_2 isotherm, surface area characterisation of subbituminous coals[20]

The BET-surface calculated from nitrogen adsorption isotherm 5 m²/g. This is rather low for coals, but represents the accessible surface in such coals rather well (Figure 45).

[20] N_2-isotherms were provided by Dr. G. Kalies, Universität Leipzig

Isopiestical data[21]

The total amount of phenol sorbed from the gas phase onto the coal sample was determined isopiestically at room temperature in a desiccator[22]. Prior to the experiments, the coal was activated at 180°C for 3 hours. The amount sorbed was determined by regularly recording the weight increase of the coal sample until a constant value was eventually reached. The values are shown in Figure 31.

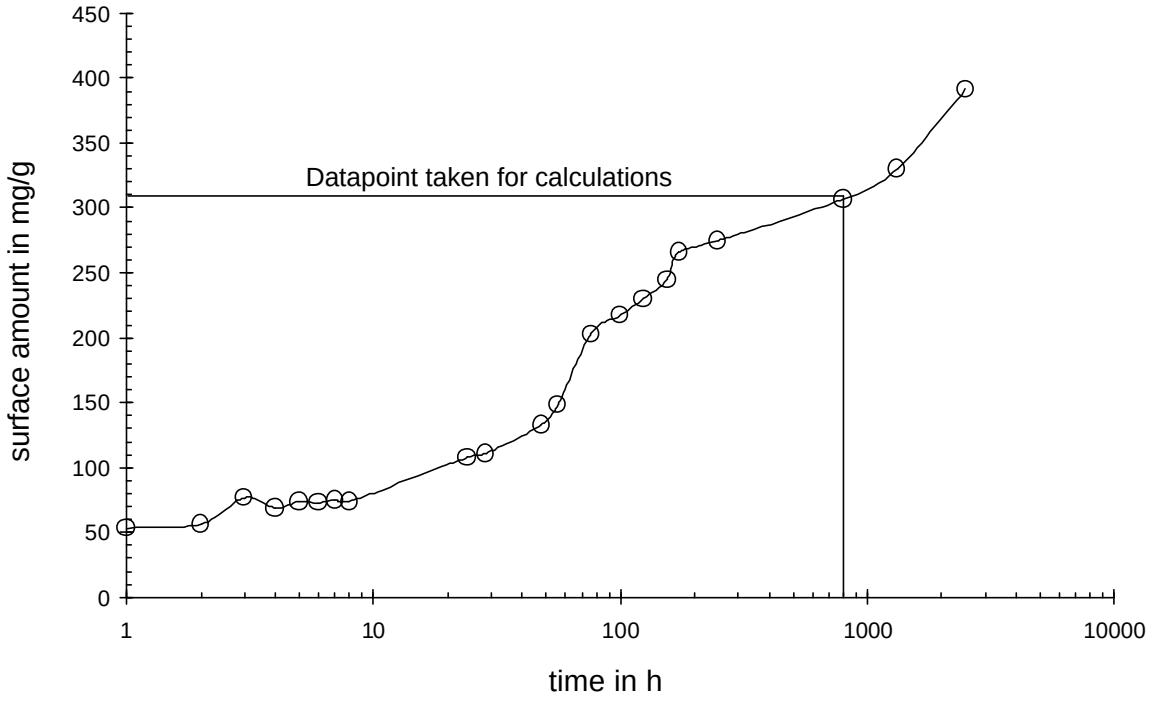


Figure 31: Isopiestical adsorption of phenol onto the subbituminous coal

The specific surface area A for the subbituminous coal sample is calculated using the limiting adsorption value G_s of phenol. After a period of 800h (G_s = 330 mg/g) it was assumed that adsorption equilibrium had established. The molar surface area *a* of pure phenol was calculated at 0.1944 m^2/µmol from the equation presented in KNAPIKOWSKI *et al.* (1996)[23] which gave a specific surface area of 682 m^2/g[24]. The calculated area is much higher than the one determined by the N_2-adsorption method (A_{BET} = 5 m^2/g). The

[21] isopiestical: constant vapour pressure
[22] Isopiestical data were provided by Prof. Dr. U. Messow, Universität Leipzig
[23] $a = 1.208 * 10^8 * V^{2/3}$
[24] 194.4 m^2 : 94.1 mg (Phenol) = x : 330 mg/g yields A = 682 m^2/g

deviation is even greater considering continuos recording which indicates that even after 5000 hours equilibrium is not achieved.

$$d = \frac{a\,\Gamma_S}{A_{BET}} = \frac{194.4\ \frac{m^2}{mmol}\quad 3.5\ \frac{mmol}{g}}{5\ \frac{m^2}{g}} = 136 \qquad [5]$$

Using the surface area from the N_2-BET-Plot, it becomes apparent that 136 layers (*d*) will have accumulated after 800 hours (Equation 5). Beyond 800 h the curve still rises which implies that even more layers will build up.

This mismatch of BET and isopiestical data for phenols needs to be expected. The isopiestical measurements were carried out at room temperature at which phenol is still a solid but close enough to its melting point and can therefore exhibit a substantial vapour pressure. The phenol could now condense at the coal and build up several layers. Such a behaviour has been described for the water air interface of phenolic solutions at room temperature by neutron reflection studies which showed phenol aggregates of more than one layer (LI *et al.* (1998B)). Further, MESSOW *et al.* (1986) generally attributed the mismatch between BET and isopiestical data to the different temperatures used in the two methods as well as the different time scales applied in the experiments.

5.3.2 Coarse sand

The coarse sand was purchased from a drilling company in Baden-Württemberg and has a grain size of 0.71-1.25 mm. The sand has been treated (washed, burned, rounded, 97.5% quartz) according to the requirements in DIN EN 12904. It is certified to be free of organic matter.

BET-N_2 data yield a surface area well below the detection limit of 0.5 m^2/g. Approximation of the surface area from the medium grain size by treating the grains as sphere yields 19 cm^2/g. Overall, the surface area is rather small. Isopiestical data show only little adsorption of phenol, which may be within the error bars of the applied method.

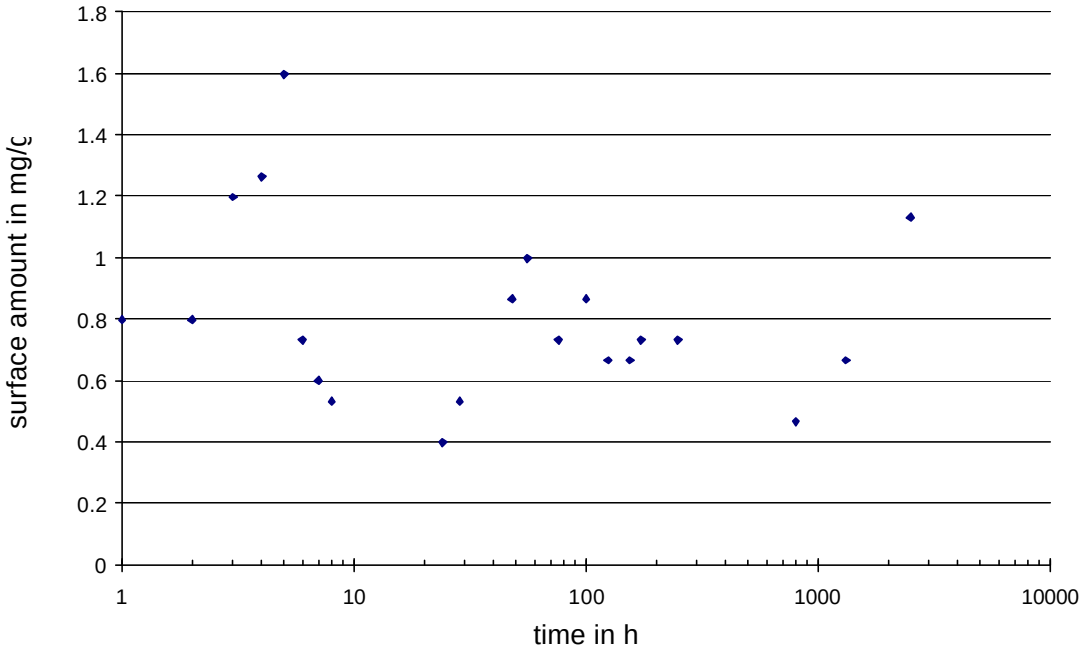


Figure 32: Isopiestical adsorption of phenol onto the coarse sand

5.3.3 Dolomite

Two dolomite samples were provided by Rehberg (UFZ). XRD data confirm that both samples are identified as dolomite (spectra can be found in appendix III).

The dolomites are obtained from the *Zechstein* formation sampled in a quarry south of Leipzig. According to Rehberg, these carbonates represent the type of rock predominant in the contaminated deep aquifers in the vicinity of Deuben well. For this reason the two dolomites were chosen as model adsorbents to evaluate the retardation of SCAP at that site (chapter 7.3). The dry dolomite samples were pulverised in a ceramic ball mill for 30 minutes. The powder was furthermore sieved through a fine mesh screen (0.085 mm). The obtained pulverised samples were dried again at 100°C for 2 days and kept in a desiccator until used.

DEGAS-Data[25]

As described in the previous chapter, the natural organic matter (NOM) proportion in sediments and rocks dominates their adsorption capacity. The precise analysis of NOM in

[25] DEGAS-Analysis (Directly coupled Evolved Gas Analysing System) were carried out and data were provided by Dipl. Chem. Ch. Schmidt, FSU Jena.

dolomite samples is crucial. It cannot be done by the differential method (TC-IC=TOC), since IC is with more than 98% the dominating TC source. An often applied method is eliminating the IC by washing the sample with acid and analysing the remains for TC, which in this case equals the TOC fraction. The acid washing procedure was performed as follows. Approximately 30 mL of HCl (30%, p. A.) were added very slowly to 4g of pulverised sample placed in a 250 mL round bottom flask. After the vigorous effervescence had ceased another 20 mL of HCl and a magnetic stir bar were added. The system was allowed to stir for 1 week. After a settle time of 1 day the remaining sediment was filtered off, dried and weighed back. Evolved gas analysis (EGA) analysis confirmed the complete removal of carbonate (IC) by procedure. Results from TOC determinations from the cold acid extract show that Limestone II may have a 10 times higher TOC value than Dolomite I has (data were provided by S. Leider UfZ). This would be in agreement with their observed adsorption capacities. Nonetheless, this high TOC difference of the two dolomite samples appears rather questionable, since the TOC mass traces from the DEGAS data differ less than 1%.

The pulverised dolomites and the remains of their acid extract were analysed as described in SCHMIDT & HEIDE (2001). Gas analyses were carried out using a specific device of high-temperature mass-spectrometry (DEGAS, directly coupled evolved gas analysing system). The system comprises a NETZSCH STA 429 thermoanalyser coupled directly to a Balzers QMG 421 quadrupole mass spectrometer. Measurements were carried out under vacuum of 10^{-4} to 10^{-3} Pa using a linear heating rate of 10 K/min in the temperature range 20 to 1450°C. The mass spectrometer was operated at 100 eV in a multiple ion detection mode for some selected mass to charge (m/z) ratio. The system runs under highly non-equilibrated conditions thus hindering reverse reactions of the evolved volatiles to occur.

The cold acid extract remains data do not differ by an order of magnitude for the two dolomite samples (Figure 33). Although the applied method does not allow to determine a TOC value in the two samples, it can be concluded, that they have a similar TOC.

As shown from the adsorption experiments (Figure 49, page 85), the adsorption capacity of the two dolomites differs significantly. Dolomite II has a much higher adsorption capacity than dolomite I. This observation may be due to a different TOC distribution across the sample. This could be confirmed by DEGAS (Figure 34-Figure 36).

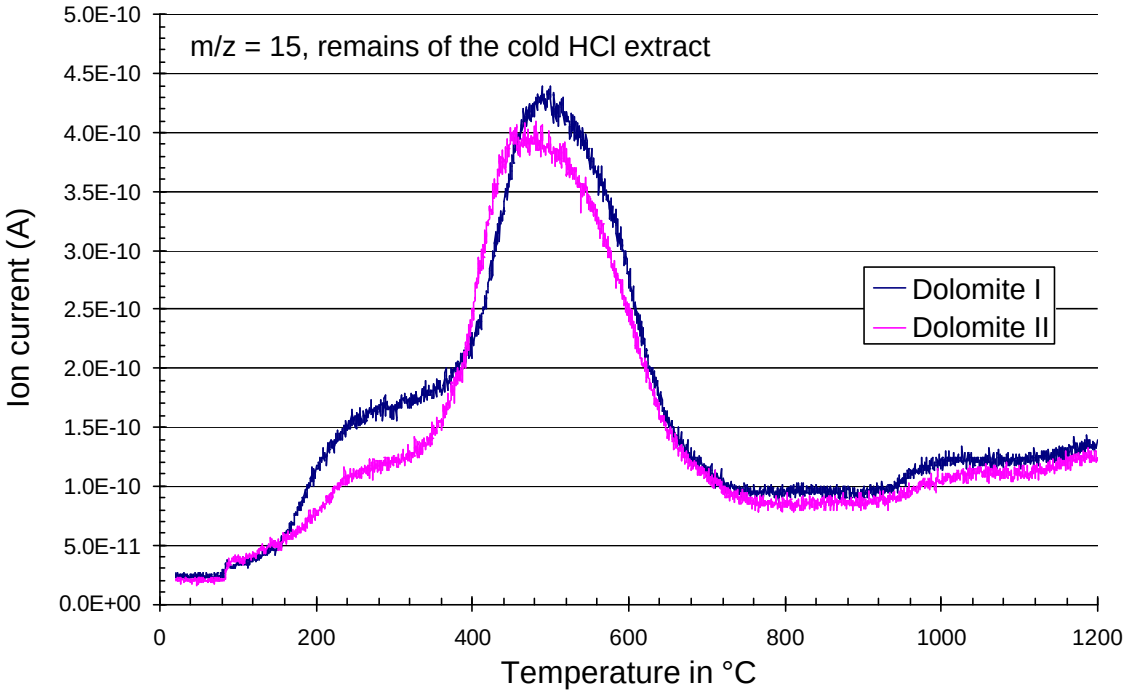


Figure 33: Bulk TOC comparison for the remains of the could acid extracts

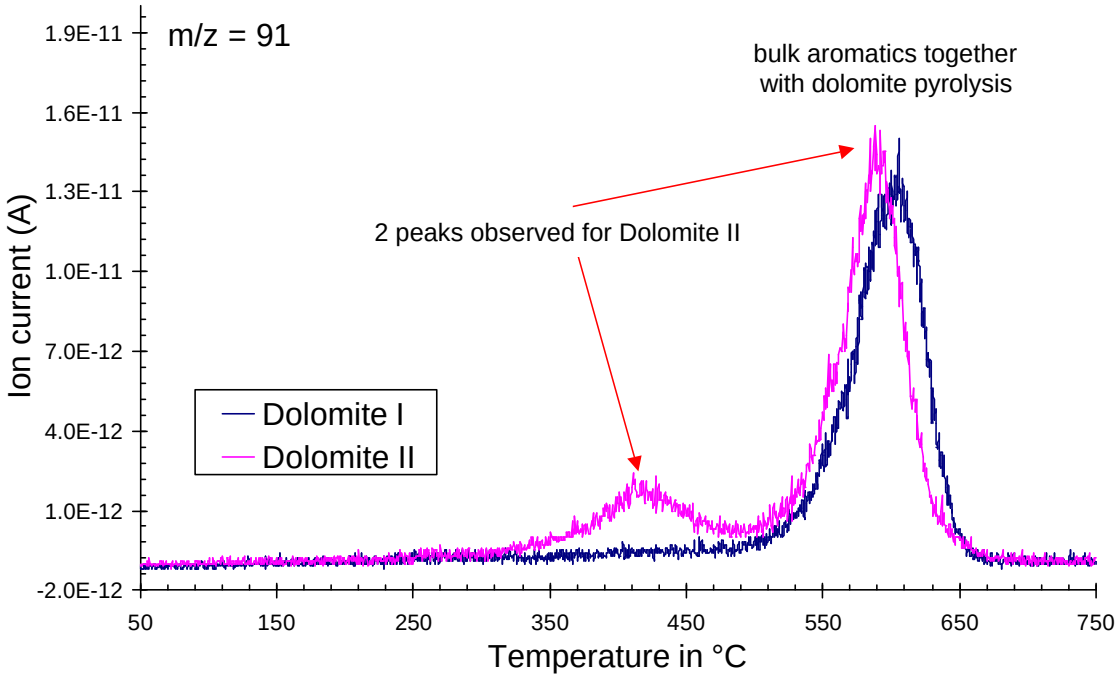


Figure 34: Aromatic TOC comparison for the pulverised dolomite samples

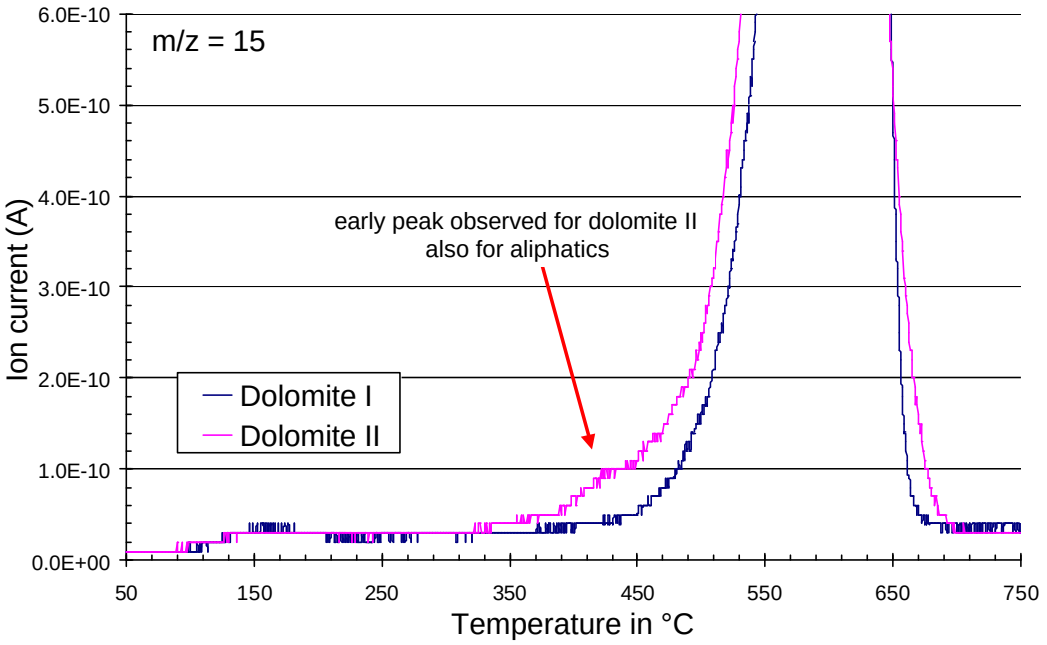


Figure 35: Aliphatic TOC comparison for the pulverised dolomite samples

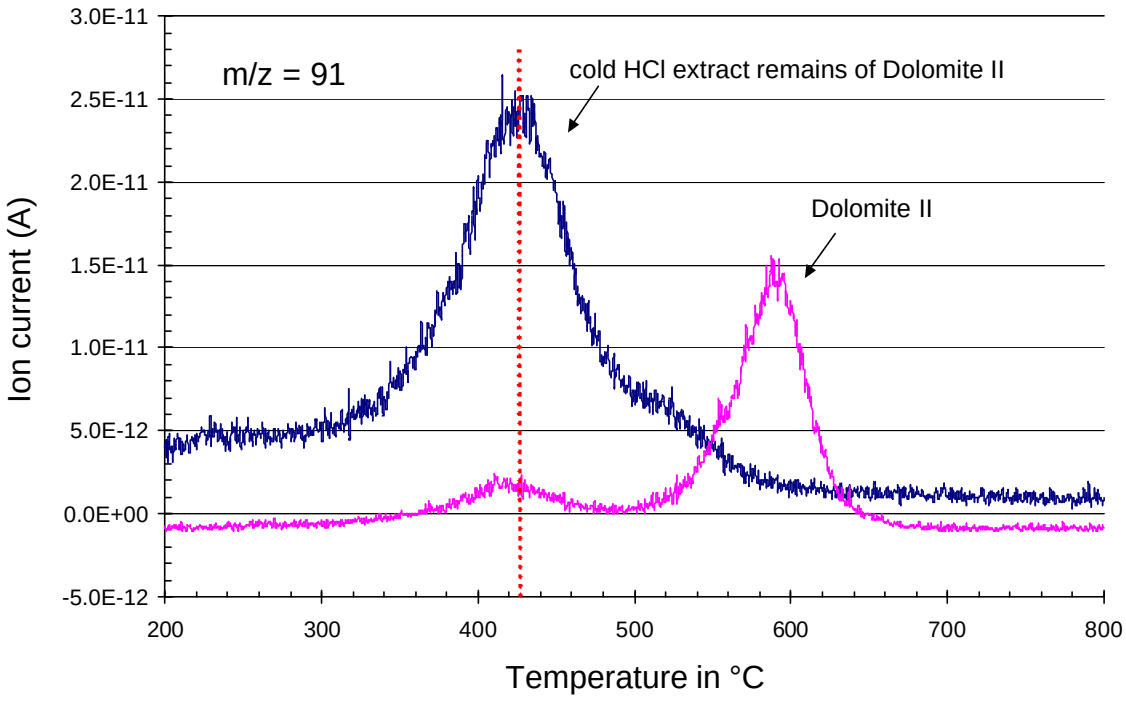


Figure 36: Comparison of extract remains and pulverised dolomite aromatic TOC

The main organic matter is released, when the carbonate structure is thermally broken down, which is indicated by high CO_2-signal occurring at the same temperature as the aromatic indicator peak (m/z=91). This indicates, that the organic carbon released under these conditions must be trapped in the carbonate structure and cannot freely be accessed by surface processes.

For Dolomite II, an early peak occurs at the same temperature as in its acid treated

complementary (Figure 36). This indicates the presence of organic matter on the surface of the carbonate which can be accessed by surface processes.

This difference is further confirmed by XRD data. The dolomite peak of dolomite II has a lower intensity than that of dolomite I. This signal suppression may be caused by the organic matter present on its surface.

Nitrogen adsorption isotherms and isopiestical data

The experiments have been carried out under the conditions as described in chapter 5.3.1 at the University of Leipzig. The nitrogen adsorption isotherm method (BET) yields for both dolomites a surface area of less than 0.5 m^2/g. A more detailed surface area can not be reported since it is below the detectable area.

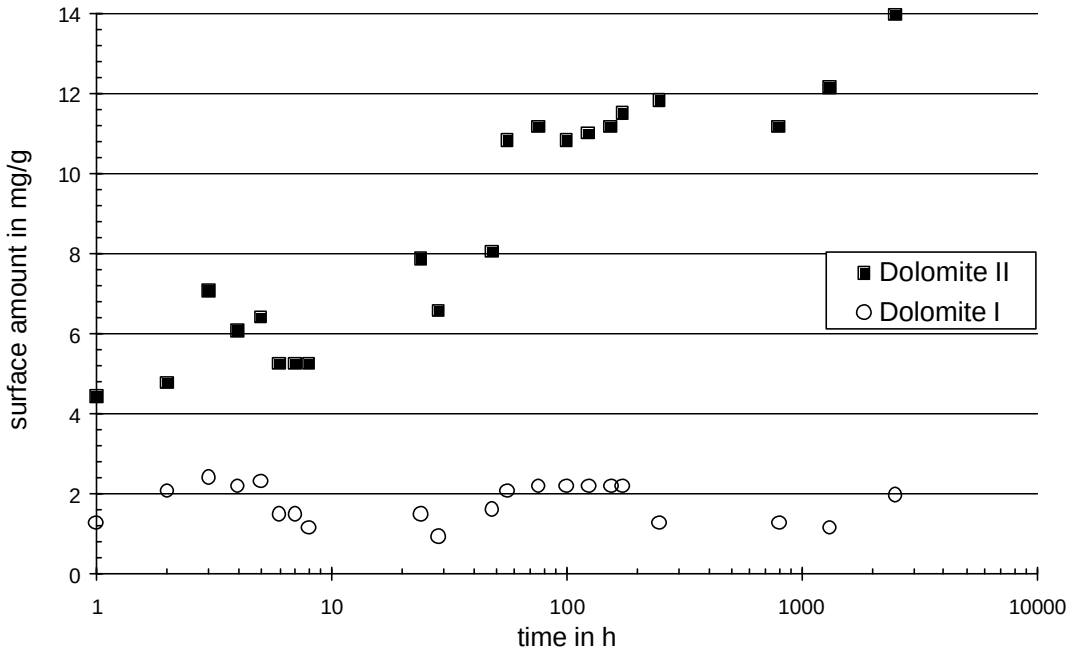


Figure 37: Isopiestical adsorption at room temperature (RT) of phenol onto the dolomitic samples

Isopiestical data show a significant adsorption for dolomite II, but virtually no adsorption for dolomite I (Figure 37, Figure 38). For dolomite Ⅱ, a similar graph as for subbituminous coal is observed and it is concluded, that a similar multi-layer coverage occurs. Presuming 136 layers will yield a specific surface area of 0.17 m^2/g for dolomite II, which is approx. 20 times less than the specific surface area of the subbituminous coal used. No surface area can be given for dolomite I, since the approximation does not seem to apply.

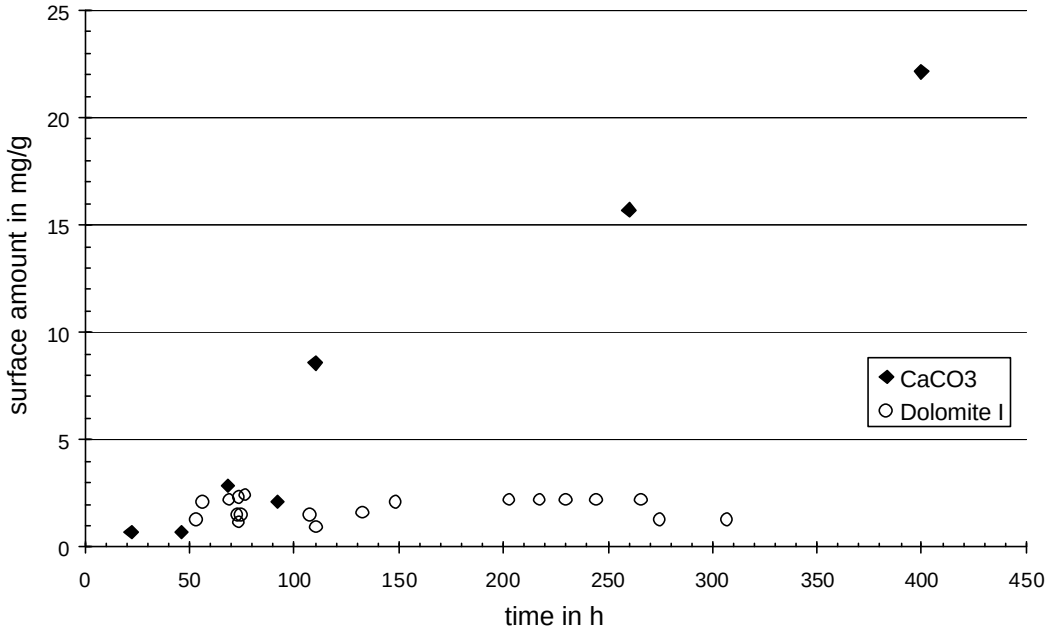


Figure 38: Isopiestical adsorption at RT of phenol onto the dolomite I and $CaCO_3$

5.4 Investigations on the total adsorbed amount[26]

The total adsorbed amount can be a very valuable parameter for further thermodynamic interpretations as well as for the interpretation of the adsorption mechanism. This total adsorbed amount is not accessible from dilute solutions since they almost only allow the estimation of the surface excess amount. Isopiestical data represent the total adsorbed amount and are a preferred method for their determination.

The total adsorbed concentration of phenol and trimethylphenol onto subbituminous coal gained in two individual isopiestical studies at room temperature are shown in Figure 39. At the start, the surface amount for both phenols is similar. After 1 day (20-30 hours) the phenol curve rises well above the trimethylphenol curve. This may indicate that phenols condense in several layers (689 layers at 800 hours), as expected before.

A reason for this different behaviour of the two phenols may originate from their vapour pressure, which is 40.7 hPa for phenol and 0.02 hPa for 2.4.6-trimethylphenol. This reduces the rate at which the trimethylphenol layers could build up since its concentration

[26] All isopiestical data were supplied by the working group of Prof. Dr. U. Messow, Universität Leipzig and were carried out using the provided adsorbents.

is much lower in the gaseous phase and a still rising curve indicates a much slower build up. A further reason for this different behaviour of the two phenols may result from the adsorption mechanism itself. Assuming that adsorption of further layers is caused by the interaction of the hydroxylgroups from the phenols, than a sterical blockage of this group by e.g. neighbouring alkylgroups may result in fewer layers to be built up. This may especially apply to 2.4.6-trimethylphenol, where the hydroxylgroup is sandwiched by 2 methylgroups.

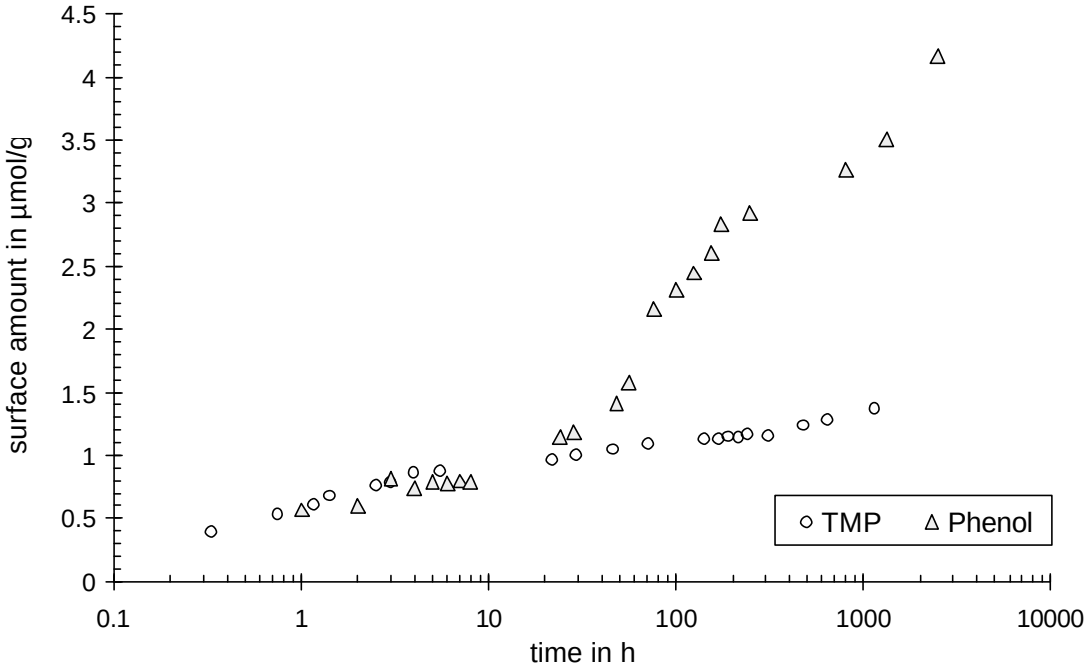


Figure 39: Isopiestical isotherm of phenol and 2.4.6-trimethylphenol onto coal

The following experiments were carried out to investigate the interaction existing for the adsorption of phenol from its aqueous solution. For this reason the total adsorption of water, phenol and methanol (as a reference) on subbituminous coal, sand and both dolomites was studied.

The isopiestical isotherms for methanol, water and phenol onto subbituminous coal are shown in Figure 40. The isotherms can be interpreted based on the respective vapour pressure data. The two liquids (methanol and water) start with comparable surface amounts. While the methanol curve steadily rises, the water curve does not rise much and eventually crosses the phenol isotherm after 100 hours. These findings would predict that phenol is preferentially adsorbed from its aqueous solution and can replace the water film existing on organic matter within aquifers.

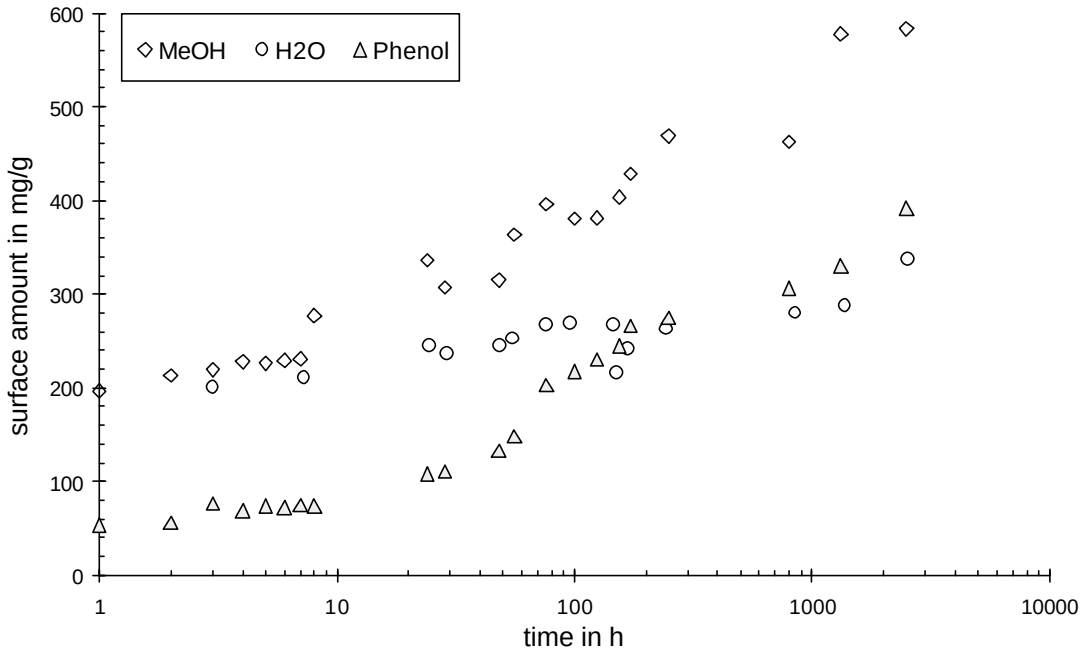


Figure 40: Isopiestical studies of methanol, water and phenol on coal

The isopiestical isotherms for methanol, water and phenol onto coarse sand are shown in Figure 41. No significant adsorption was observed. The water and phenol isotherms are close to each other. This would predict, that neither water nor phenol would preferentially be adsorbed from an aqueous phenol solution.

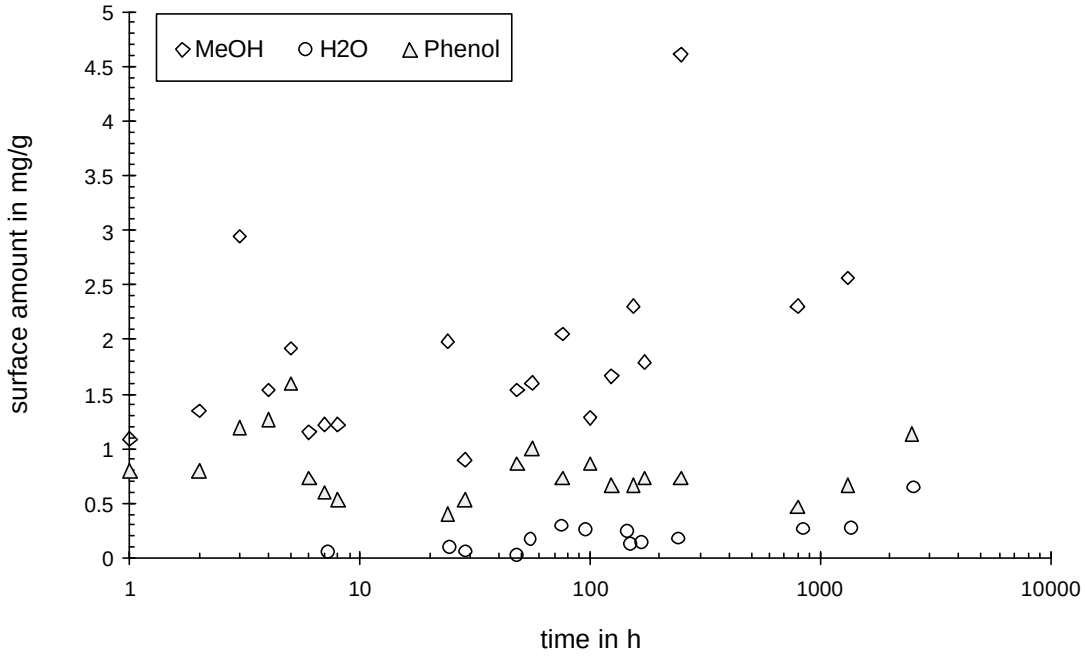


Figure 41: Isopiestical studies of methanol, water and phenol on coarse sand

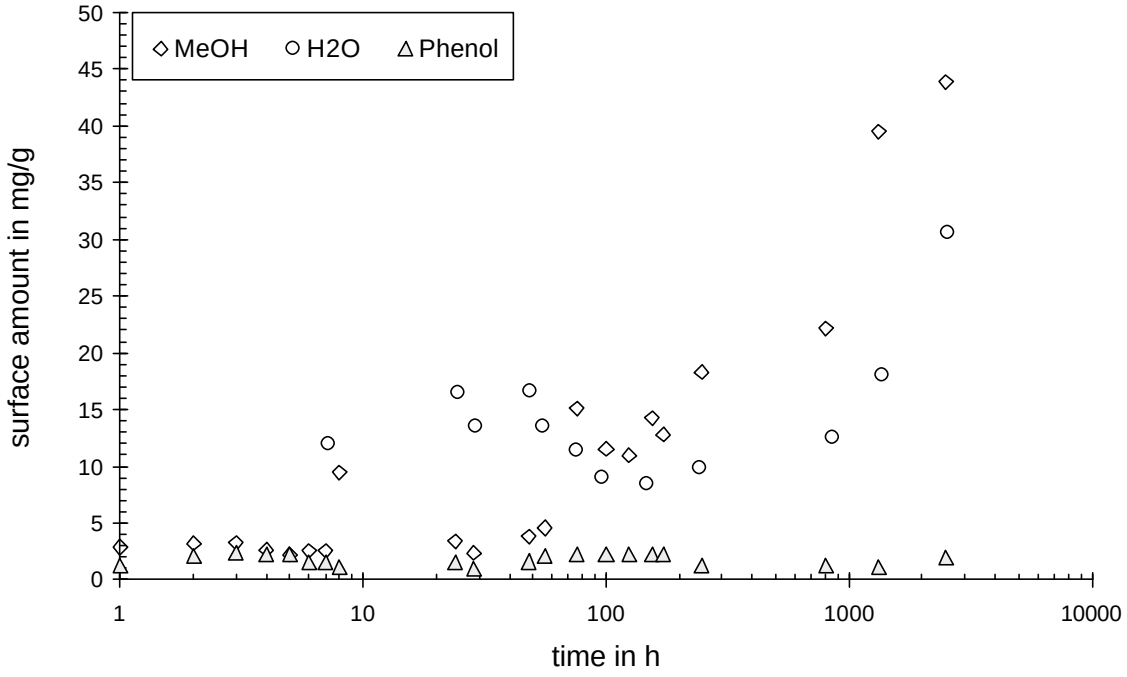


Figure 42: Isopiestical studies of methanol, water and phenol on dolomite I

The isopiestical isotherms for methanol, water and phenol onto the dolomite I are shown in Figure 42. The behaviour of water and methanol with respect to this adsorbent is reversed to their behaviour on subbituminous coal. Phenol is virtually not adsorbed by this dolomite sample. Water on the other hand is rather well adsorbed. Those findings would predict, that water is preferentially adsorbed from an aqueous phenol solution resulting in a negative SEI for phenol.

The dolomite II sample (Figure 43) shows no real preference of any of the three adsorptives for the first day. After 100 hours phenol and methanol are preferentially adsorbed. This changes at 1000 hours, when the water curve rises and crosses the phenol curve. This behaviour could be explained by a very inhomogeneous surface which consists of organic matter and uncovered dolomite. The organic matter prefers phenol and methanol, while the dolomite surface prefers water. Depending on how these materials are exposed to the vapours this behaviour could result. Those findings would predict, that phenol could preferentially be adsorbed from its aqueous solution. This however, strongly depends on the distribution of the organic matter on the dolomite surface.

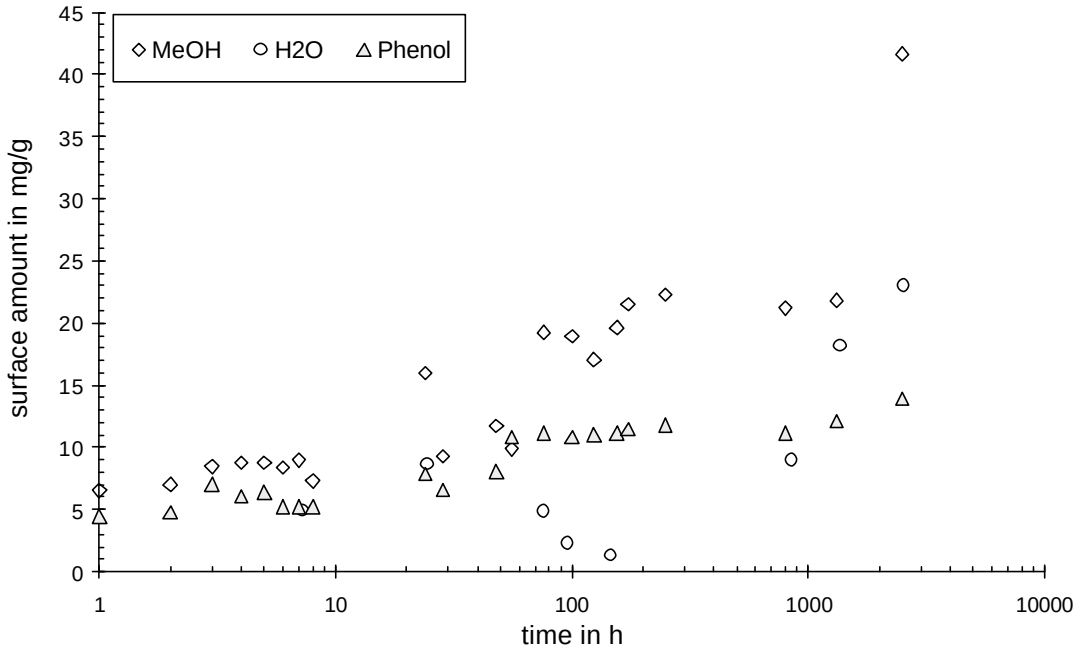


Figure 43: Isopiestical studies of methanol, water and phenol on dolomite II

5.5 SCAP adsorption from their aqueous solution

Several preliminary laboratory experiments showed a spread of the distribution coefficients for the various SCAP compounds of about a factor of 50 between phenol and the lowest soluble SCAP class propylphenols (also compare Tab. 2, p. 8). In order to demonstrate the adsorption mechanism one SCAP compound was selected from those preliminary experiments. This will be 3.4-dimethylphenol. It is believed that this SCAP represents an average adsorption behaviour of all SCAP.

5.5.1 Experimental

The experiments were conducted as batch experiments which have been successfully applied to the investigation of adsorption mechanisms as reported by e.g. ARNARSON & KEIL (2000), KARAPANAGIOTI *et al.* (2000), RÜGNER *et al.* (1999), XIA & BALL (1999), JARDINE *et al.* (1989). The phenol solutions were prepared by accurately weighing in a stock standard for each selected SCAP in methanol to a final concentration of 1000 mg/L per SCAP. Aqueous phase buffered solutions were prepared from the methanol stock solutions. Those buffers should maintain the pH at a constant value during the experiment. The following buffers with their respective ionic strength (I) were applied:

- pH 4: citric-acid-phosphate buffer after McIlvaine, I= 0.24
- pH 6: citric-acid-phosphate buffer after McIlvaine, I= 0.33
- pH 8: phosphate buffer after Sörensen, I= 0.20

Sodium azide at a concentration of 500 mg/L was added in order to inhibit bacterial growth. Methanol concentrations in the aqueous solutions were always less than 0.5% (vol/vol), a level at which methanol is known to have no measurable effect on the adsorption process (NKEDI-KIZZA *et al.* (1987)).

The experiments of the various solid materials were conducted as follows.

dolomite samples: Approximately 7 g (exact weight recorded) of the pulverised sample was placed into a 22 mL screw top amber vial. Exactly 15.5 mL of the subsequent aqueous phenol-buffer solution was added.

sand-subbituminous coal-mixture: Pulverised subbituminous coal and sand (filter sand pre-washed with acetone, grain size 0.71-1.25 mm) were mixed thoroughly and 15.5 g of this mixture placed into each 42 mL screw top amber vial. Exactly 31 mL of the subsequent aqueous phenol-buffer solution were added.

sand, subbituminous coal: Exactly 77.1 mg of subbituminous coal and 15.423g Sand (filter sand pre-washed with acetone, grain size 0.75-1.25 mm) were weighed into each 42 mL screw top amber vial. Exactly 31 mL of the subsequent aqueous phenol-buffer solution were added.

control vials containing no solids: For each phenol concentration, two separate vials were filled with 31 mL (big vials) /15.5 mL (small vials) of the phenol-buffer solution with no adsorbent added. Those vials always represent the start concentration c_0 under storing conditions. Errors during storage are minimised in this way.

After the phenol-buffer solution has been added, the vials were immediately sealed with Teflon faced butyl rubber septa. The vials were stored at 11 °C in the dark and shaken vigorously by hand at the start and every 24 hours until sampling. All experiments were carried out in duplicate/triplicate. After an equilibration time of 5 days the aqueous phase was sampled by opening the vials and withdrawing a small aliquot (2 mL) of the supernatant buffer. The samples were centrifuged in 2 ml vials and where applied prior to analysis diluted to a final concentration of 2-200 µg/L. Analysis was carried out by HPLC, with the system and column described in chapter 4.2.1 on page 43. Surface excess was calculated based on the decrease of the solute concentration in the aqueous phase from the vials with the adsorbent present relative to the control vials.

5.5.2 Results and Discussion

Sand + Subbituminous coal

To provide similar material as present in an unconsolidated quaternary aquifer, sand and subbituminous coal were mixed in the ratio 99.5%/0.5% wt/wt. This ratio was chosen as it represents equal surface areas for the two solids.

From individual experiments carried out for pH 4, 6 and 8 over a wide concentration range (10-10000 µg/L phenol) no phenol adsorption was observed for the coarse sand. This is in agreement with the isopiestical data (Figure 41). Thus, observed adsorption can solely be attributed to the added coal.

Preliminary experiments, which have led to the development of the transport parameter PCF (chapter 6.2) were carried out on a pre-mixed adsorbent. Although care was taken, the difference in grain size by a factor of 10 inevitably forced the separation of the two materials (sand + subbituminous coal) present in the pre-mixed adsorbent and thus the ratio for the two materials was not constant in all batch experiments.

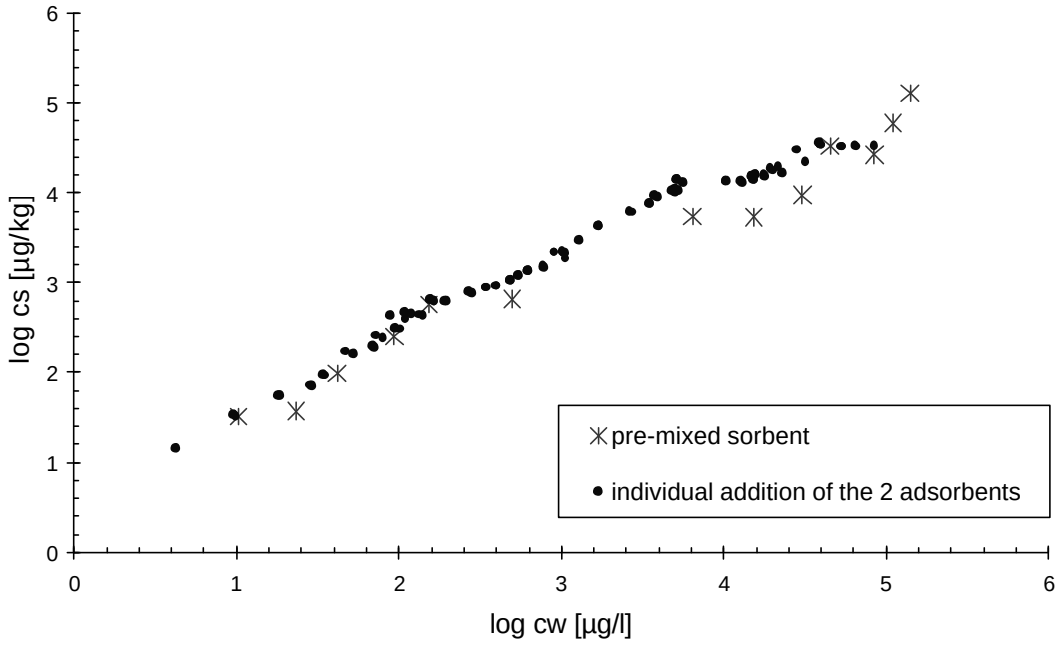


Figure 44: SEI of 3.4 DMP at 11°C and pH 8 on pre-mixed adsorbent vs. individual addition

An investigation on the adsorption mechanism has been made by means of a highly resolved isotherm (Figure 45) for 3.4-dimethylphenol on individually added subbituminous coal and sand at pH=8. This SCAP was chosen since its adsorption properties towards this adsorbent represents the mean value for all SCAP as tested in preliminary experiments (C0 is less adsorbed while C3 are better adsorbed than 3.4-dimethylphenol). Additionally, the hydroxylgroup on this chosen SCAP is not ortho-blocked by an

alkylgroup. As preliminary experiments showed, the isotherms for ortho-blocked alkylphenols are not as clearly defined.

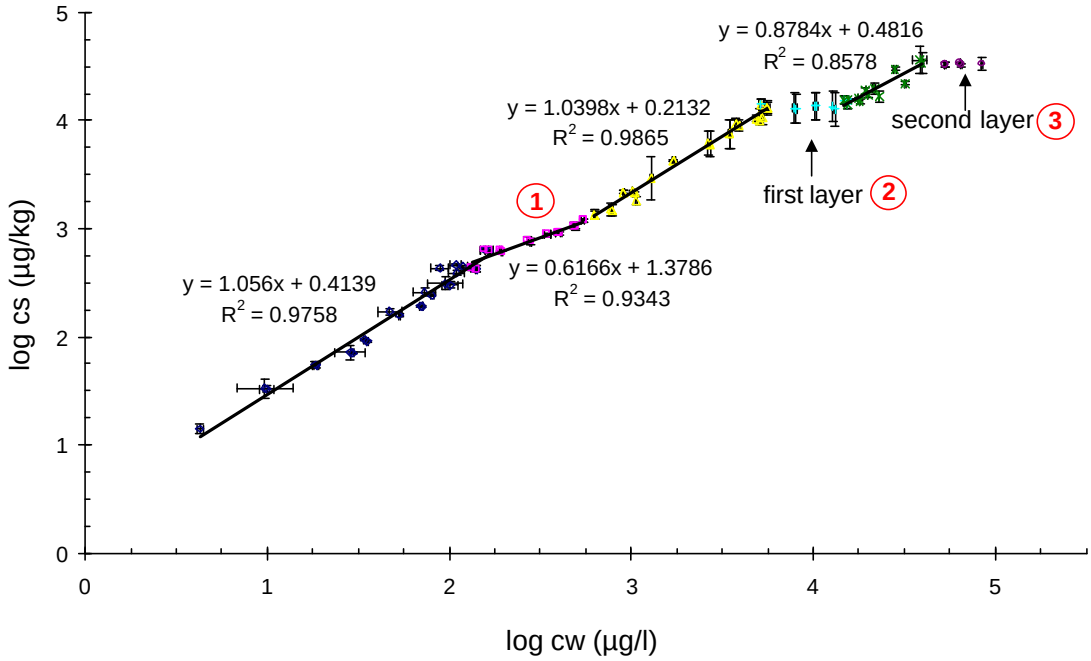


Figure 45: SEI of 3.4 DMP at 11°C and pH 8 on subbituminous coal/sand

The error bars in Figure 45 were calculated using the Gaussian error distribution function and the standard deviations from 3 HPLC determinations:

$$\Delta x = \sqrt{\left(\frac{v}{m}\Delta c_0\right)^2 + \left(\frac{v}{m}\Delta c_W\right)^2 + \left(\left(\frac{c_0 - c_W}{m}\right)\Delta v\right)^2 + \left(\left(\frac{(c_0 - c_S)v}{m^2}\right)\Delta m\right)^2}$$

$\Delta v = 0.1$, $\Delta m = 0.001$

As apparent from Figure 45 the isotherm can be divided into 6 sections, each represented by individual Freundlich parameters. The first section, represented by the equation y=1.056x+0.4139, has a Freundlich exponent very close to 1. This indicates a monofunctional and unspecific interaction of DMP with the coal surface which is best achieved when the DMP molecules lie flat on the coal surface as indicated Figure 28 (A). When the phenol concentration in solution increases, the coal surface becomes more and more “crowded” and at a threshold concentration the phenol molecules overcome this crowded state by changing their orientation. This transition state is indicated in Figure 45 by a decreased slope ① which represents a state with lying and standing phenol molecules present at the surface. The further filling with only standing phenol molecules (Figure 28 (B)) is characterised by an unspecific interaction, as indicated by a Freundlich exponent very close to 1 which is almost identical to the one from the first section of the isotherm. This filling is continued until a mono-layer coverage is observed which is

indicated by a plateau within the isotherm②. The mono-layer coverage was furthermore verified by the surface area derived from the BET-N_2-isotherm together with the area required by a single 3.4-dimethylphenol molecule. The hydroxyl group belonging to the sorbed phenols is directed towards the water. Via hydrogen bonds a water film consisting of 2 to 4 layers of water molecules is aggregated around the phenol layer (PESCHEL *et al.* (1978)). It is obvious, that some driving force is required to replace the water molecules from the first layer by further phenols and this can only be achieved at a higher phenol threshold concentration. Then slowly a second layer builds up. It is noticeable, that the Freundlich exponent (0.8578) from this part of the isotherm equals approximately the mean of the second (0.6166) and the third part (1.0398) of the isotherm. This supports a double layer second coverage as indicated by Figure 46. From thermodynamic interpretations, the hydroxyl groups of the first layer must interact with hydroxyl groups of the second layer and also the second layer must direct their hydroxyl groups towards the water. However, since only one hydroxyl group is present in the phenol molecule, double layer coverage becomes apparent. The data however suggest that the second layer is represented by a 2.5 times coverage. This leads to the fact that only 4 out of 5 molecules from the first layer function as anchor molecules in the building of the second layer, which is a double layer having hydroxylgroups at either end. In this way, hemimicelles[27] form in the second layer thus stabilising the whole layer. The concentration range beyond the second coverage was not investigated. However, from isopiestical data it can be concluded that further layers may build up as the concentration in the water increases.

The long term stability of these hemimicells was tested by preparing 22 identical batch samples of the highest concentration (100 mg/L) and ten blank samples. Over a period of 100 days, every 10th day 2 vials were sampled and discarded afterwards. The samples were frozen and analysed at the end of the experiment. No change in adsorbed concentration with time after the 3rd day was observed. Since the adsorbed mass did not further increase with time a diffusion process into a micro-porous media will not be dominating (intraparticle diffusion). This is also supported by the fact, that the adsorbed phenol layer supports the hydrophobic coal to stay in solution by providing hydrogen bonding contact to the water. This mechanism may be regarded similar to micell formation.

[27] Hemimicelles are interfacial aggregates of surfactants and co-surfactants. SCAP are co-surfactants (FLEIG (1995), PATRICK *et al.* (1999)).

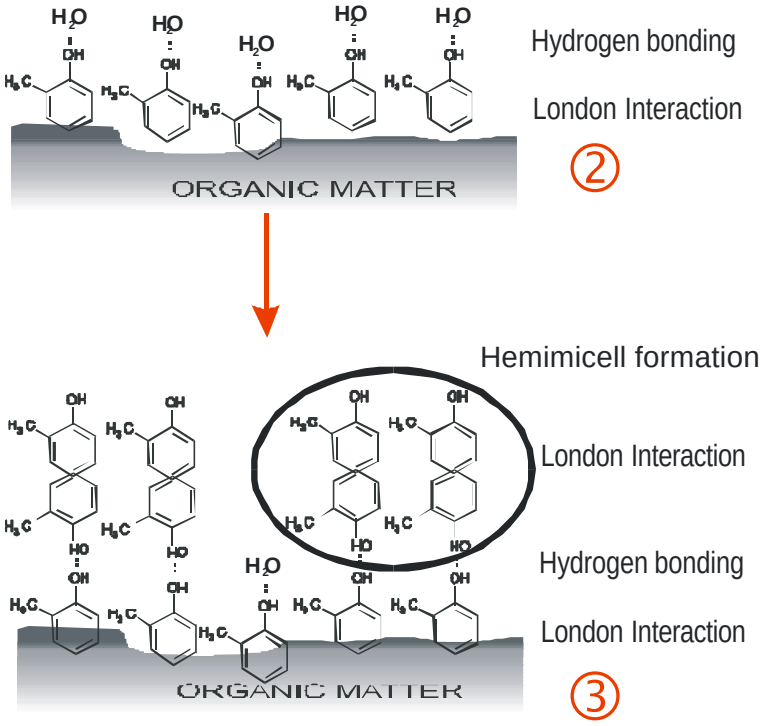


Figure 46: Sketch of the suggested SCAP adsorption mechanism onto organic matter

The layers beyond the first layer may be much easier displaceable in desorption experiments than the first layer. FINDENEGG *et al.* (1983) report about the lower adsorption energy that is observed for layers beyond the mono-layer coverage. This may also be expected for the aqueous phenolic solution / subbituminous coal system and can here be assigned to the different forces and interaction mechanisms present between the coal and phenol as well as between the mono-layer and the layers beyond.

The factors influencing the adsorption of phenols from aqueous solution onto carbon may be predominantly the ionic strength and the pH of the solution. The influence of the ionic strength has been discussed by PESCHEL *et al.* (1978). Unlike SETSCHENOW (1889) they distinguish between ions that strengthen the water aggregate structure (Na^+) and ions that weaken the water aggregate structure (K^+). Since the buffers used in own experiments contain both ions in similar concentrations, the influence of the ionic strength is probably minimised. As explained earlier, the influence of the ionic strength on polar substances is not really significant. The pH influence seems more important since phenols are weak acids (chapter 2.3, page 6). This influence becomes dominant, when the second layer forms. At higher pH values (pH 12) phenols are deprotonised (negatively charged) and a second layer cannot build up on the basis of hydrogen bond interaction (Figure 47) and also repelling forces of the deprotonised hydroxylgroup prevent a further build up of layers. This is in agreement with DIVINCENZO & SPARKS (2001) who investigated the different adsorption mechanisms of charged and uncharged pentachlorophenol onto soil. It is furthermore supported by investigations of MADHUKUMAR & ANIRUDHAN (1994) who describe the phenol exchange characteristics of sediment samples from coconut husk retting. They

report a general decrease in the adsorption capacity of organic material with increasing pH. On the basis of own experiments this can be interpreted as a mono-layer coverage. A decrease of the adsorption capacity has also been described by those authors with decreasing pH and can also be explained by a mono-layer coverage.

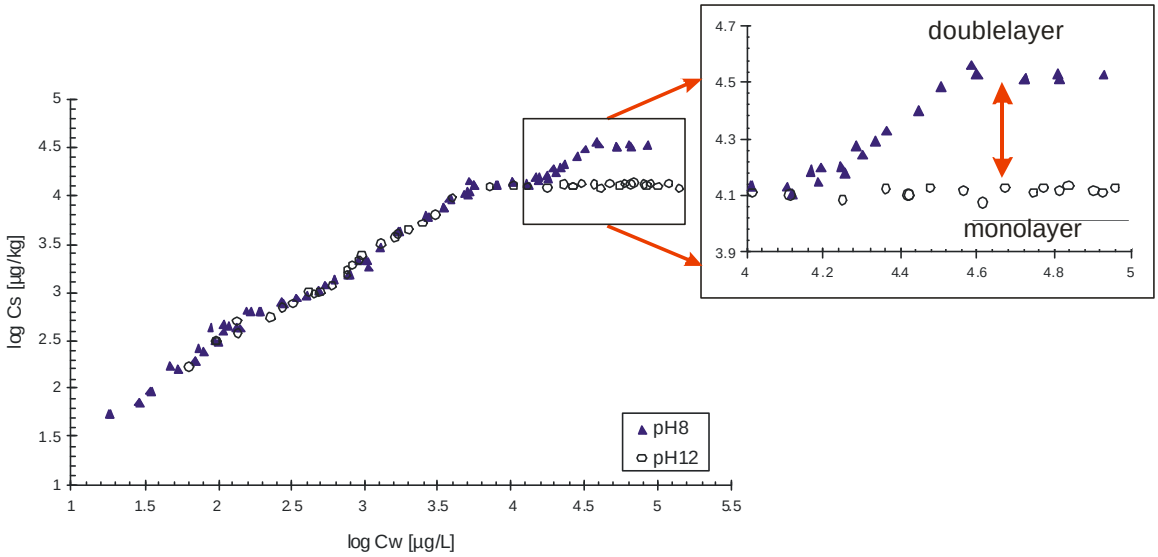


Figure 47: SEI (11°C) of 3.4 DMP at pH 8 and pH 12 on subbituminous coal/sand

Dolomite

The two ground dolomite samples could be characterised as different with respect to their distribution of organic matter (also compare chapter 5.3.3). Dolomite I contains the organic matter more or less only within its dolomite natrix, while dolomite II shows the presence of organic matter at its surface. Isopiestical studies suggest that no adsorption of SCAP onto dolomite I occurs from aqueous solution. However, a positive surface excess for SCAP may be observed under certain surface conditions. The adsorption properties of dolomite I in aqueous solution of SCAP strongly depend on the dolomite surface protonation (respectively: surface charge). Own investigations give evidence of a negative surface excess for SCAP at pH 6 (Figure 48), which changes to a positive surface excess at pH 8 (Figure 49). Unfortunately, the zero point of charge of dolomite I was not determined. Literature data[28] indicate a ZPC between 6.5 and 8.5 supporting the observed adsorption behaviour. This finding further implies that the pH margin in which a positive surface excess for SCAP occurs lies between the ZPC of the dolomite and the

[28] lyre.mit.edu/3.52/2001/chapter9.pdf, 23.09.2002

acid constant (pKa) of the respective SCAP (also compare Figure 50). For groundwater relevant pH conditions the SCAP adsorption onto dolomite can be described as negligible.

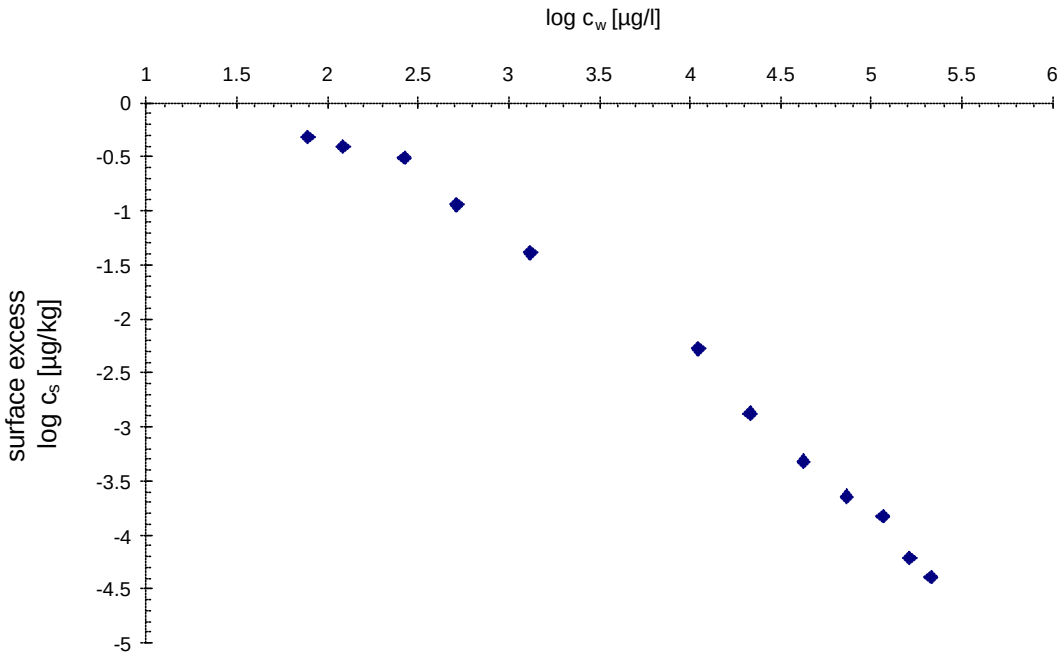


Figure 48: Negative SEI for phenol adsorption onto dolomite I, pH 6

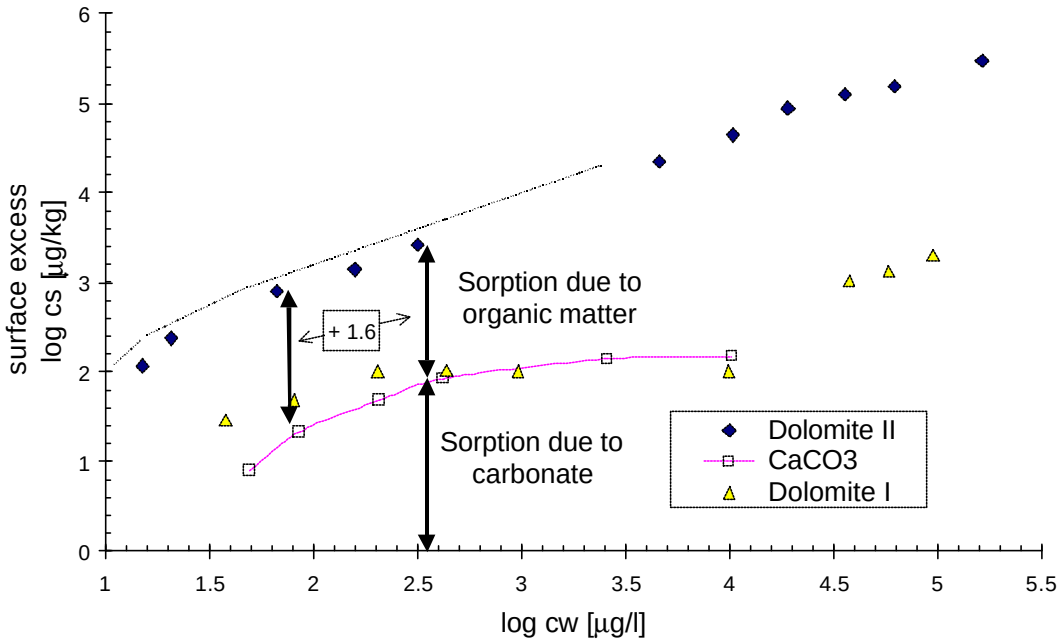


Figure 49: SEI of 2.4 DMP at 11°C and pH 8 on carbonates

The adsorption behaviour for 2.4-dimethylphenol onto both dolomites and calcium carbonate powder (p. A.) at a pH of 8 is shown in Figure 49. Pure calcium carbonate also shows some adsorption capacity for phenol from aqueous solution at this pH, possibly caused by hydrogen bond interaction. Unfortunately, no organic free dolomite could be provided since dolomitisation is a secondary mineral forming process. However, calcium carbonate appears to represent similar adsorption properties to dolomite at pH 8. More

important however is the adsorption due to organic matter. For dolomite II a 40 times higher adsorption capacity is observed, which is solely attributed to the organic matter present on its surface. The lack of accessible organic carbon in dolomite I forces its isotherm onto the calcium carbonate isotherm.

The pH of the solution influences the adsorption on dolomite differently compared to the experiments on the sand/subbituminous coal samples. This furthermore suggests that the adsorption on carbonate is caused by hydrogen bridging bonds (Figure 50) and the ZPC of the material greatly influences its adsorption property. The decline of adsorption capacity at pH 6 compared to pH 8 indicates that the ZPC of dolomite was surpassed.

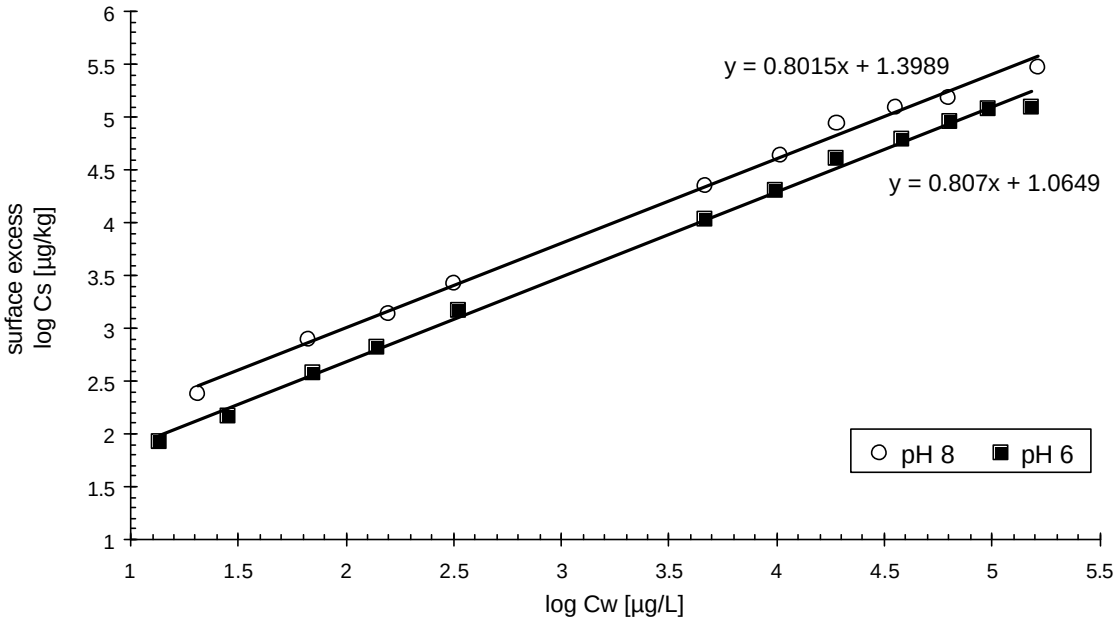


Figure 50: SEI of 2.4 DMP at 11°C and pH 8, 6 on dolomite II

All further experiments were carried out at a pH of 6, which represents the pH in the *Zechstein* formation in Deuben/Profen (chapter 7.3). Negative surface excess was solely observed for dolomite I. In the following the data for dolomite II will be presented and interpreted on the basis of the adsorption mechanism. The SEI of 5 SCAP obtained on dolomite II at 11°C and pH 6 are presented in Figure 51.

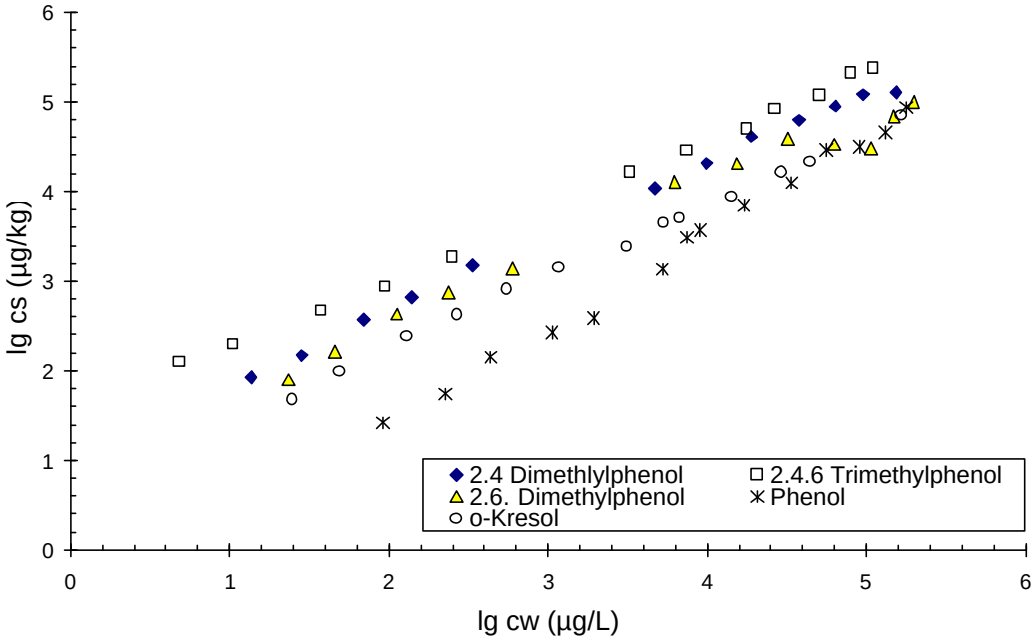


Figure 51: Isotherms of various SCAP on dolomite II at 11°C and pH 6

It is apparent from the above plot that the isotherms of the various SCAP run parallel in the concentration range log c_w 1-3, while they partly overlap in the higher concentration region. Only 2.4-dimethylphenol and 2.4.6-trimethylphenol show a different behaviour at higher concentrations compared to the other 3 SCAP. This may be due to the fact that they contain an alkyl group in opposite position to the hydroxyl group. When the phenols now change their orientation with increasing concentration in solution by "standing up" the interaction between of the aromatic ring of those two phenols must occur through the methyl group.

URANO *et al.* (1981) and MANES (1998) suggested a unit-equivalent Freundlich coefficient by normalising C_w to the water solubility of the compound as described in greater detail in chapter 5.1. This normalises solubility controlled partitioning equilibria and the resulting isotherms should plot on the same line. Any deviation suggests that the adsorption is based on specific interactions.

The solubility normalisation has been applied to the isotherms from Figure 51 and the results are shown in Figure 52. Only in the low concentration range (log c_w 1-3) the isotherms of the various SCAP fall onto the same line (A) which implies a non-specific interaction between the adsorbent and SCAP. This means that SCAP must lie flat on the dolomite surface since only in this orientation there is no great difference between the individual SCAP. When the SCAP change their orientation, the interactions become more specific and the phenols do no longer plot on a single straight line (B).

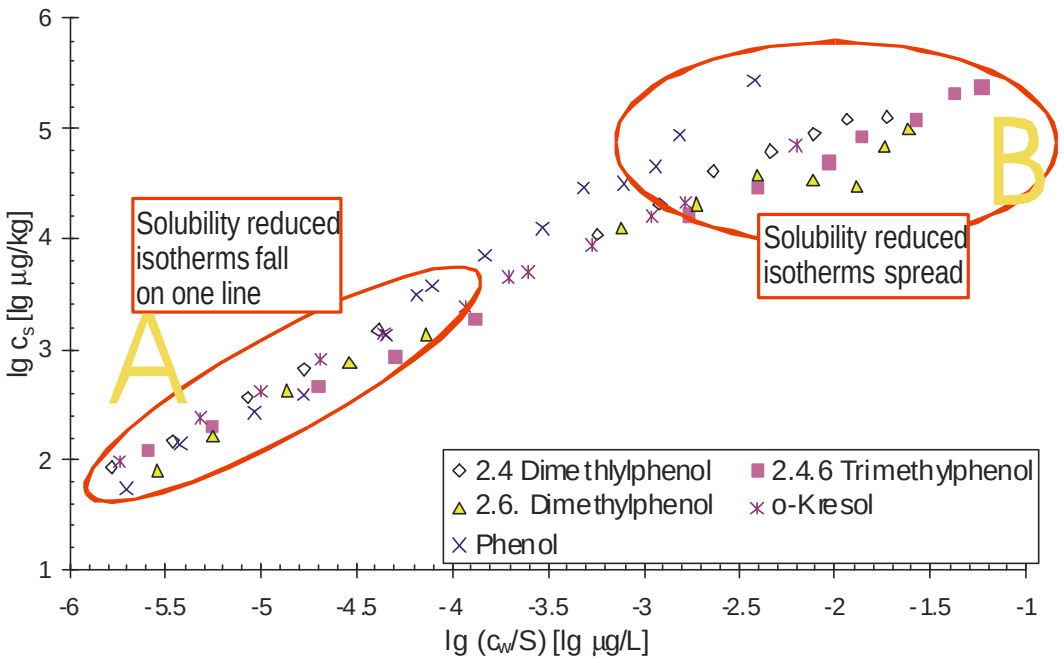


Figure 52: Solubility reduced isotherms from Figure 51

5.6 Looking back at the chapter

The adsorption of SCAP is somewhat different from commonly investigated contaminants such as PAK (RÜGNER *et al.* (1999), MOREHEAD ET AL (1986)). Therefore, their adsorption behaviour cannot accurately be described by existing partitioning models. Thus, their adsorption is commonly overestimated when described by common isotherms only.

The adsorption mechanism was investigated for SCAP. It could be shown that they adsorb in multi-layers onto subbituminous coal. The adsorbed layers stabilise themselves by aggregating to hemimicells. Thus SCAP do not show an expressed tendency to diffuse into the adsorbent and thus intraparticle sorption processes are not predominant.

Generally, the adsorption capacity is mainly assigned to natural organic matter. No adsorption was determined for coarse sand and only little adsorption was found for carbonates and dolomites. Overall, the partitioning coefficients of SCAP are very small with the consequence that they are only little retarded in aquifers. Thus, SCAP are very mobile compounds.

At groundwater relevant pH values SCAP adsorption onto NOM is not pH dependent. In contrast, the adsorption onto carbonate sediments is pH dependant due to the nature of interaction. Generally, the adsorption capacity of carbonates is observable between the ZPC of the carbonate material and the acid constant of SCAP.

6 Conceptual models on SCAP transport in groundwater

The earlier introduced chemical analytical technique (HS-SPME-GCMS, chapter 4.3, pp. 45) allows a more detailed investigation of SCAP in water and sediments at contaminated sites. It enables the hydrogeochemical investigation of individual SCAP compounds in very complex matrices as present at such sites. The next chapter describes two transport parameters which have been derived from site and laboratory investigations. They are furthermore supported by experiments described in literature. These parameters should assign some properties of reactive tracers to SCAP (CAIN *et al.* (2000), DAVIS *et al.* (2000)). From their distribution at the site, a long-term prediction of the groundwater and contaminant pathway, the type and age of contamination and some prediction about its further development should be derived. The parameter development is demonstrated with a simple 1-D transport modelling approach to investigate the impact of the nature of the steplike phenol isotherm on its transport behaviour in aquifer systems.

The derived and theoretically described parameters can be found applied in chapter 7.

6.1 Modelling the steplike phenol isotherm

The applied model code SMART (Streamtube Model for Advective and Reactive Transport, Universität Tübingen), a one dimensional Lagrangian streamtube model was chosen because the steplike phenol isotherm can be easily integrated. The parameters chosen for the model runs simulating the 1D transport through a column filled with sand and subbituminous coal (99.5/0.5 % wt/wt) are summarised in Tab. 18.

Tab. 18: Applied model parameters

Length [m]	1
Diameter [m]	0.11
Discharge [l/h]	0.36
Eff. Porosity	0.15
Velocity [m/s]	7.3E-05
Dispersivity [m]	0.005
Dispersion coefficient [m/s^2]	3.6E-07
time step length [sec]	600

The initial concentrations were chosen below a mono-layer coverage (part ② in Figure 45 on page 81), at the mono-layer coverage and at the double-layer coverage. The resulting breakthrough curves are compared to the breakthrough of an ideal tracer and the Freundlich approximation (Figure 53).

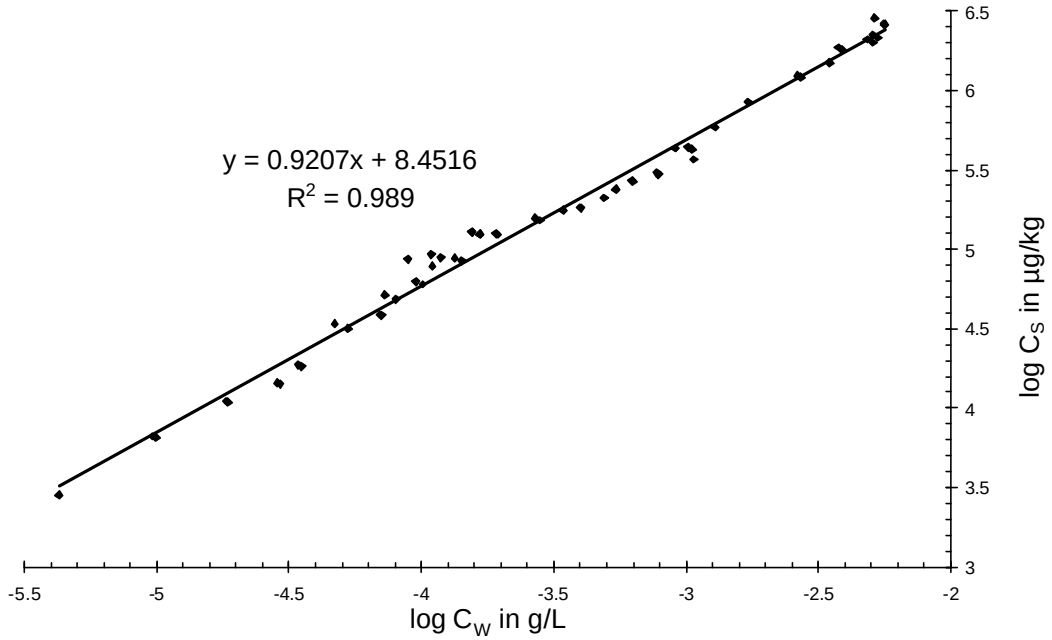


Figure 53: Freundlich approximation of the phenol isotherm (below mono-layer coverage)

The significant deviation of the breakthrough curves derived from the phenol steplike isotherm and its Freundlich approximation begins once the mono-layer coverage is achieved (Figure 54).

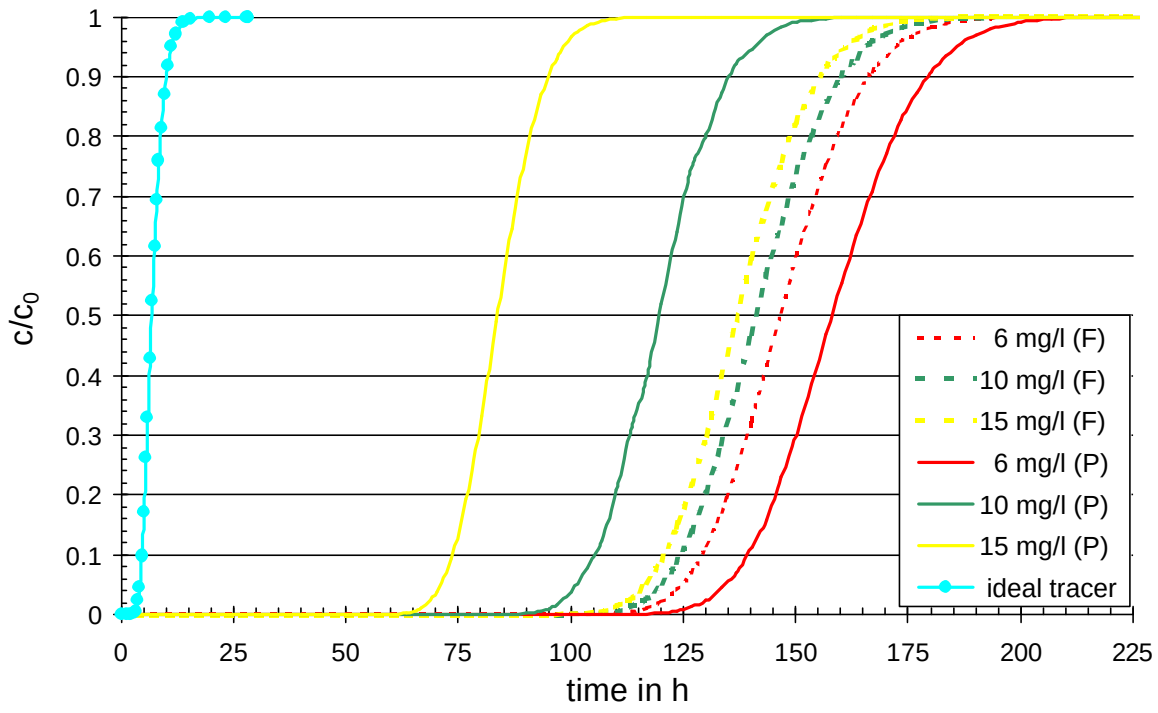


Figure 54: Breakthrough curves for ideal tracer and total SCAP input concentrations within the first step modelled by phenol isotherm (P) and its Freundlich approximation (F, dotted line)

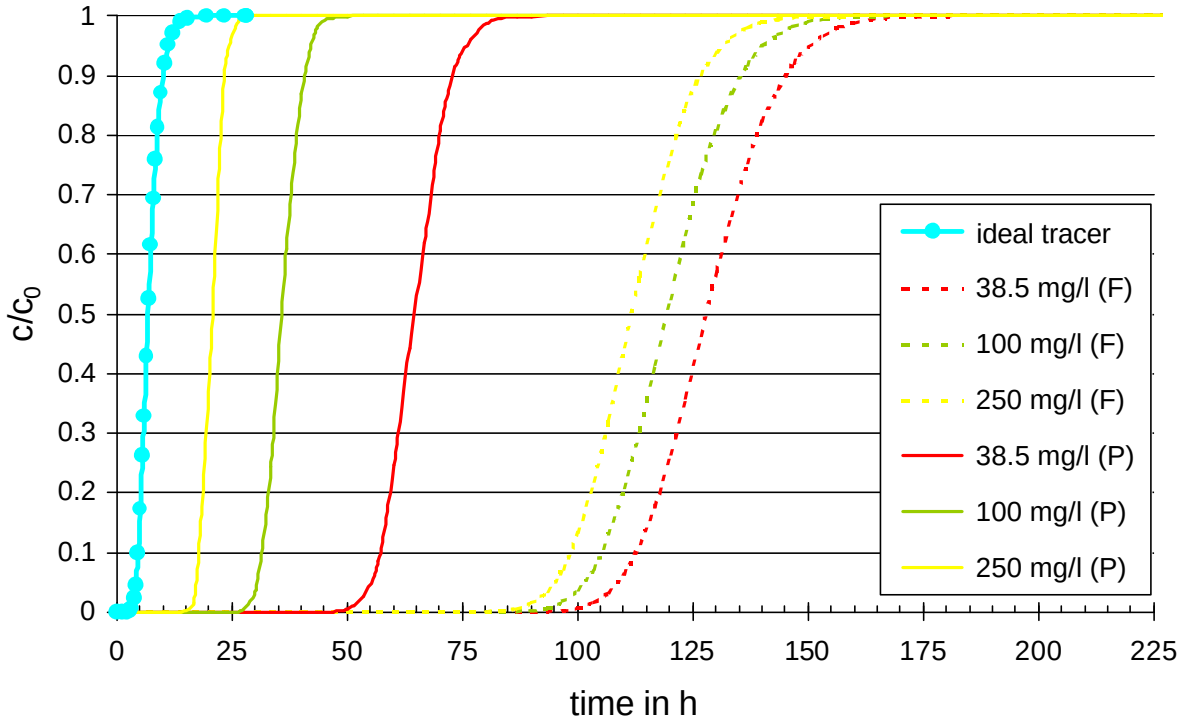


Figure 55: Breakthrough curves for ideal tracer and several input concentrations within the second layer coverage modelled by phenol isotherm (P) and its Freundlich approximation (F, dotted line)

The breakthrough curves for 3 input concentrations within the second step of the phenol isotherm (part ③ in Figure 45 on page 81) are shown in Figure 55. Generally it can be concluded that the higher the concentration the larger the deviation in arrival times between both isotherms (F & P) and the earlier the breakthrough of SCAP when modelled on the steplike isotherm after a mono-layer coverage is achieved. This trend is expected since any SCAP at a concentration higher than the one needed for the first layer to be filled and lower than the threshold value for filling the second layer travels unretarded.

The dependency of the retardation factor on the input concentration and the two modelled isotherms is shown in Figure 56. Especially for concentrations between 30 mg/L and 100 mg/L total SCAP (within the second step of the phenol isotherm) their retardation by applying the Freundlich approximation will be overestimated by a factor of 5. The displayed results are an average value for SCAP. The effect is enhanced with C_0 - C_1 SCAP which have a lower distribution coefficient and therefore within the above concentration range a retardation coefficient below 5. Commonly investigated organic contaminants such as BTEX or PAH have retardation factors orders of magnitude higher than SCAP. It must be further expected that within a complex contamination plume such as a tar oil plume those highly retarded substances are preferentially adsorbed resulting in even lower retardation factors for SCAP close to the source.

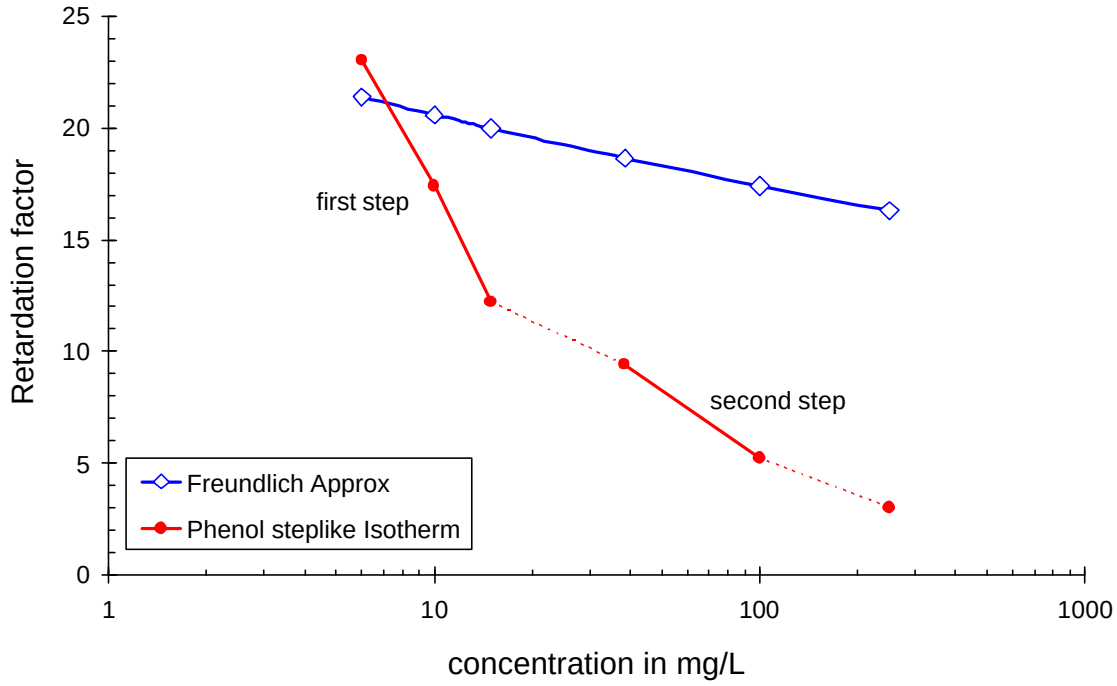


Figure 56: Retardation factors derived from steplike isotherm and its Freundlich approximation

In sum, adsorption as a natural attenuation process does not work effectively for SCAP. Commonly applied remediation systems such as “pump and treat” and also water treatment plants which are both based on activated carbon adsorber columns do not retain SCAP for a long period. Their breakthrough as toxic organic contaminants occurs quickly with the consequence that the treatment concept for these soluble contaminants must be reconsidered.

6.2 Phenol-Cresols-Fraction, PCF

As apparent from the modelling results, SCAP are very mobile compounds with rather low retardation factors. However, these properties which imply a major drawback concerning the risk due to contaminant migration can be very beneficial in the characterisation of contaminant plumes, i.e. by employing SCAP as partitioning tracers. Their rapid movement always provides fresh adsorbent material (aquifer material) to the SCAP-plume thus allowing the small difference in the C_0-C_3 SCAP distribution coefficients (compare Tab. 2 on page 8) to result in a separation of the SCAP classes along the flow path (chromatographic effect). It could be demonstrated in experiments that the Freundlich Coefficients for C_0 and C_3 SCAP on sand/subbituminous coal differ by a factor of about 50. This lead to the development of a transport parameter which should account for this difference in their retardation behaviour.

The parameter is termed phenol-cresols-fraction, abbreviated as PCF, and is defined as:

$$PCF = \frac{M_{Phenol\ [mmol/l]} + M_{Cresols\ [mmol/l]}}{\sum M_{SCAP\ [mmol/l]}} \quad [6]$$

M: molarity

Molar concentrations are used to compare the relative proportion of the SCAP compounds.

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. By applying the PCF values across a contaminated site SCAP can be used as partitioning tracers (CAIN *et al.* (2000), DAVIS *et al.* (2000)). A certain PCF furthermore typical for the SCAP source i.e. contaminated site (Tab. 19). Carbonisation plant waters derived from subbituminous coal have a PCF of approximately 0.8 while the subsequent tar has only a PCF of 0.25. This is due to the process of steam distillation in which the carbonisation plant waters are produced and also due to a higher solubility of C_2-C_3 in tar (Tab. 20). The presence of organic matter in the aquifer leads to a further separation of the SCAP classes resulting in a continuing enrichment of the plume's tip in the easily soluble and little retarded C_0-C_1 SCAP (Figure 60). The data in Tab. 19 gained from field investigations support the above statements.

Tab. 19: PCF variation with source, time and space

Anaerobic, no degradation	Input	Ageing source	Tip of the 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

Tab. 20: SCAP distribution pattern and PCF in various SCAP containing materials

Product Type	C_0-C_1 vol%	C_2 vol%	C_3 vol%	Total Phenols vol%	PCF
Carbonisation Tar	0.50	0.96	1.19	2.65	0.23
Medium Oil	12.0	7.0	3.8	22.80	0.58
Light Oil	13.7	6.1	3.8	23.60	0.62
LTC waters	1.22	0.2	0.09	1.51	0.81
Crude Oil (North Sea)	0.025	0.017	0.010	0.052	0.52

PCF variation across a plume without SCAP degradation (strictly anaerobic conditions)

The SCAP differentiation across a plume and its development over time can be expressed by the PCF. This is visualised in the next 3 figures (Figure 57 - Figure 59) by three different scenarios. LTC water which has a PCF of 0.8 acts in all three scenarios as the SCAP source. All scenarios are simulated under anaerobic conditions to minimise superimposing effects from degradation.

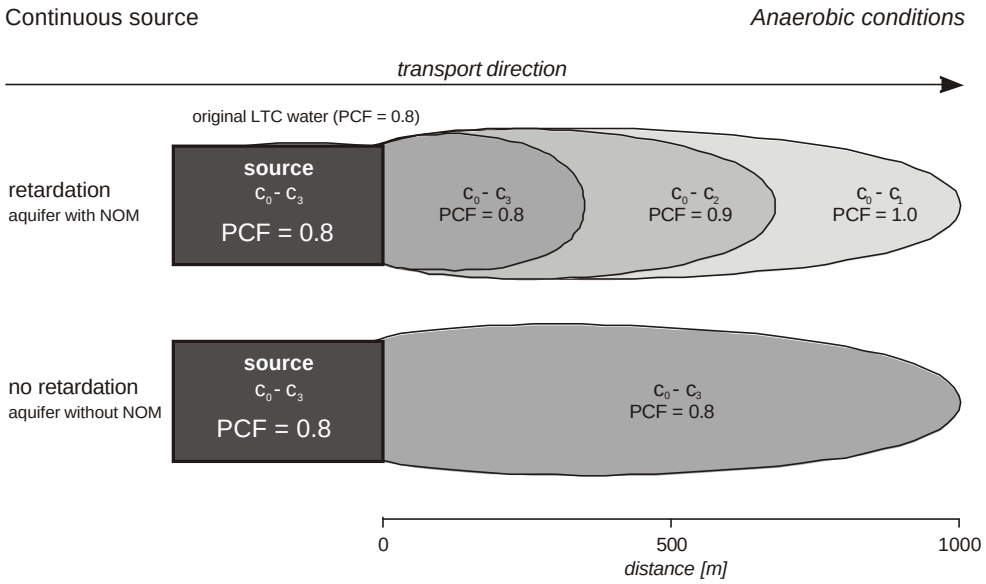


Figure 57: PCF variation depending on the aquifer system (without biodegradation)

In Figure 57 the influence of the natural organic matter (NOM) on the SCAP differentiation (PCF variation) is presented. A PCF differentiation only occurs in the presence of retarding matter (NOM) within the aquifer. Since C_0 is migrates more or less 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 number of interactions between the contaminants and the NOM surface determines the degree of differentiation. From a continuous source with a PCF of 0.8 its variation is limited to the range of 0.8 to 1.0.

A gradually depleting source due to e.g. the differential dissolution of SCAP as shown in Figure 58 has not a constant PCF over time. The source is 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. Therefore, the PCF in the source gradually decreases and may in some cases even reach 0. A decreasing PCF of the source gradually changes the starting conditions for the plume. The PCF variation across the plume simultaneously increases until it eventually covers the whole range of PCF starting with 0 at the source and ending with 1 at the plume tip. A short lived source behaves similarly (Figure 59).

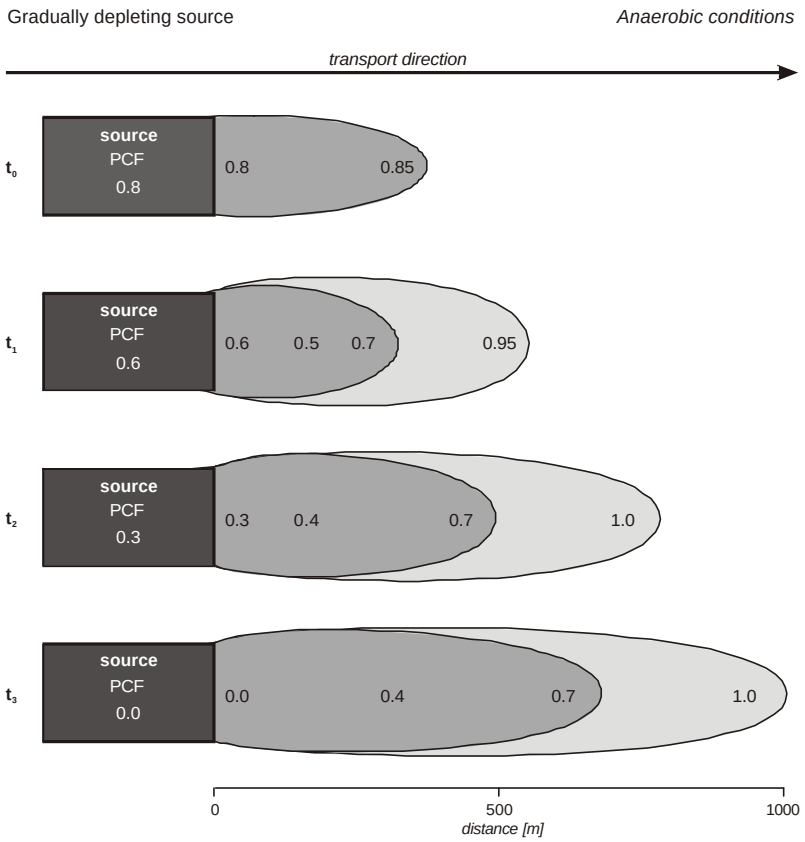


Figure 58: PCF change in the plume from a gradually depleting source over time

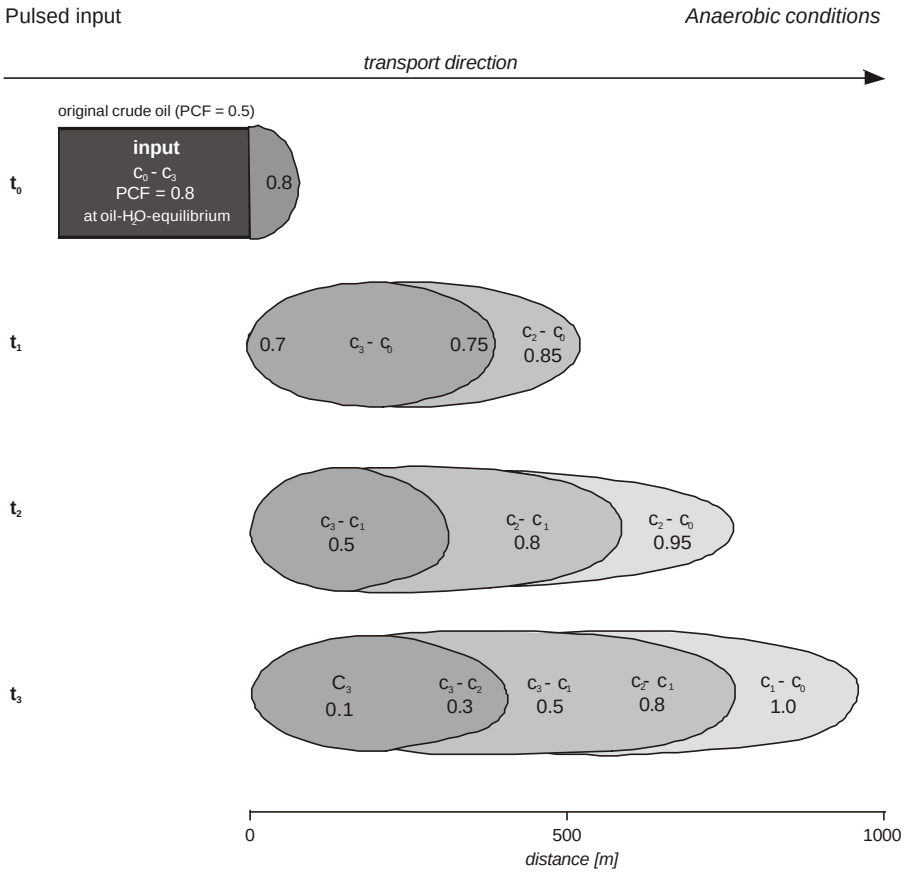


Figure 59: PCF change in the plume from a short lived source

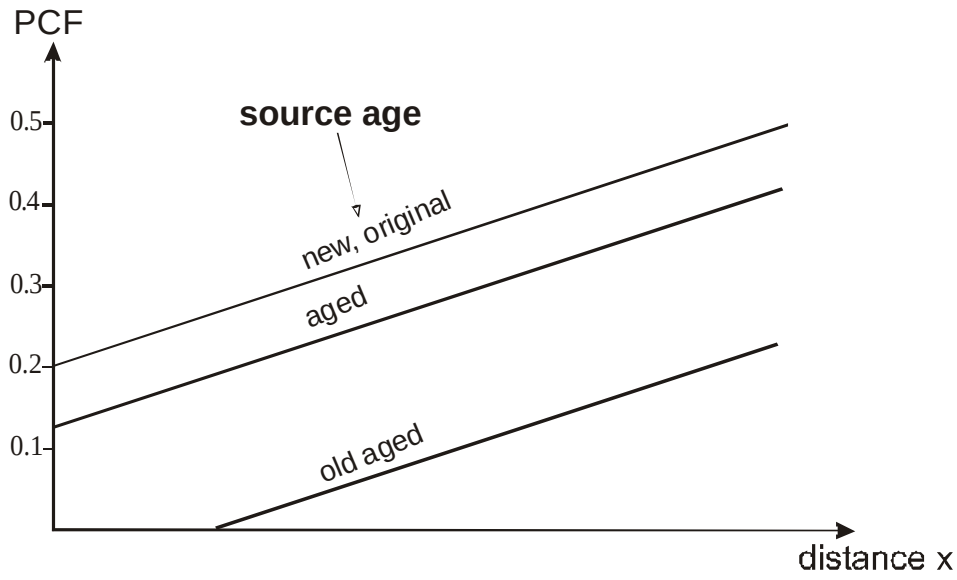


Figure 60: PCF variation across a tar contaminated site over time

A suggestion on the observable PCF in a coal tar contaminated site with distance (x) from the source and with age of the source is shown in Figure 60. The plot is a synthesis of theoretical considerations and field observations. The straight lines in the plot are very schematic. In fact, they are likely not straight.

PCF variation across a plume with SCAP degradation

The following statements are derived from theoretical studies and could not yet be supported by field data from the sites investigated in this study due to their complex nature. Once a contamination enters an aquifer the redox condition changes and a redox zonation develops (Figure 61). Close to the source sulphate reduction/ methanogenic conditions evolve. Beyond the source and the plume aerobic conditions can still exist. Fast travelling contaminants such as SCAP can leave the reducing zones and may be degraded in the aerobic zone.

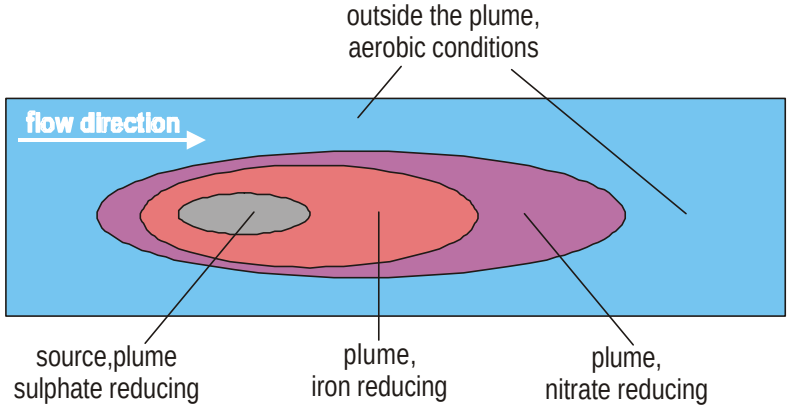


Figure 61: Redox zonation around a plume in an aerobic aquifer

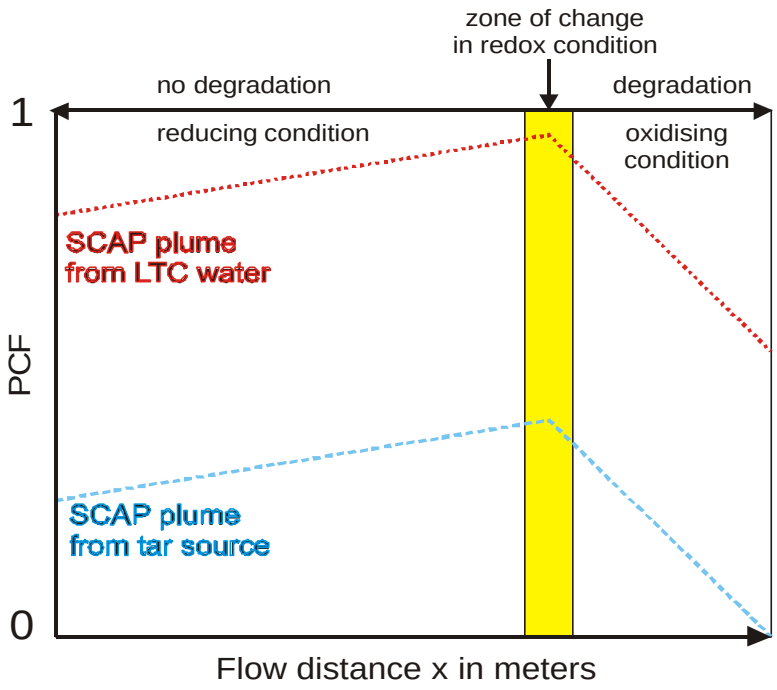


Figure 62: PCF variation within a plume at a certain time with biodegradation

According to the degradation studies summarised in Tab. 9 (p. 14) especially C_0-C1 SCAP degrade rather rapidly under aerobic and nitrate reducing conditions while simultaneously those SCAP are enriched in the tip of the plume. As a consequence, the PCF rises from a source value in flow direction until the plume eventually experiences a change in redox conditions. Degradation processes, i.e. preferential biodegradation of C_0, are responsible for a decrease in the PCF value (Figure 62).

6.3 Meta Para cresol Ratio (MPR)

The formulation of a parameter which accounts for the selective degradation of SCAP is difficult. As apparent from Tab. 9 on page 14 contradicting results have been reported for most SCAP. At the same time this degradation parameter must not be superimposed by the PCF data and furthermore the SCAP used for this parameter must be well investigated and almost always present within the contamination plume. Only cresols fulfil those requirements.

For m- and p-cresol GRBIC-GALIC (1990) report a different degradation pathway under aerobic conditions. The methyl group on the aromatic ring of p-cresol provides a site for an initial oxidative attack by **water-derived oxygen**. This results in the production of p-hydroxybenzoate which is then decarboxylated and enters the phenol pathway. The methyl group on the aromatic ring of m-cresol is not initially oxidised before ring cleavage. Radiolabel studies show that the methyl group is mainly converted to methane. Initially m-cresol is carboxylated forming o-methyl-hydroxybenzoate which is then believed to undergo ring cleavage followed by β-oxidation to acetate. Since m- and p-cresol have

almost identical physico-chemical properties (Tab. 2, page 8) their ratio can only be affected by aerobic degradation. Thus, the ratio of m- and p-cresol may very selectively indicate the presence of oxygen even if oxygen is only temporarily present. The MPR (meta-para-cresol ratio) will be defined as:

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

By the above definition oxygen is indicated in a rising MPR well above 10. Since such data may be able to average out along a flow path, this parameter can be more selective than reference date measurements.

7 SCAP in the subsurface- case studies

In the following chapter the distribution of SCAP at 3 field sites is illustrated and interpreted together with supplementary data from those sites. Each field site has been selected to cover a broad range of different conditions and contaminant scenarios in order to draw a broad picture about the behaviour of SCAP in the subsurface. The cases differ as follows:

a) Geology	b) Source of Contamination	c) Typ of SCAP-Source
• alluvial valley fill aquifer • tertiary sandy aquifer • deep carbonate (carstic) aquifer	• gasworks site • tar processing plant/ tar oil lakes • deep well disposal of LTC waters	• LTC water • tar/ tar oil • point source • diffuse source

Unfortunately, no access was gained to a well investigated field site without ongoing remediation scheme installed and with a shallow contamination in a rather homogeneous aquifer.

The sampling was carried out together with consultants or site owners within the context of their sampling scheme. All samples were analysed by the author and carried out in triplicate with the HS-SPME-GCMS method as described in chapter 4.3. The geological and hydrogeological background information and other chemical analytical data not including the phenolindex were provided by the site owners or as stated otherwise. More data are summarised in the Appendix.

7.1 Shallow contamination in an alluvial aquifer at a gasworks site

For the geological and hydrogeological description of the site the unpublished report from ARGE NUKEM DRESDEN (1995) has been used. Further data were provided by HPC Gera.

7.1.1 Introduction to the field site

The site was in operation until the early 1990s. It produced town gas from subbituminous coal (brown coal) and has an area of ca. 50,000 m^2 (200 by 250 m). The site is situated on alluvial deposits in a SW-NE directed syncline adjacent to a river and is additionally covered by a 2 m thick anthropogenic fill deposited during plant operation. The typical unconsolidated alluvial sediments such as loam, gravel and boulder represent the local aquifer and are found up to 7 m bgl with varying thickness of unconsolidated material. The bedrock (aquitard) comprises Devonian phyllites and intrusive gabbroic and dioritic rocks.

The contaminant flow direction is towards a river and may influence the surface water quality. In October 1994 the following depths to the water table were measured: 1.53 m at monitoring well 13 (inflow) and 3.03 m at monitoring well 14 (outflow), which represents a rather shallow water table. The main groundwater flow direction is NNW to SSE. The aquifer can be described as slightly confined. It is highly transmissive and has a hydraulic conductivity of $1.4*10^{-4}$ m/s and a water velocity of approximately to 1 m/d (n_e=0.06).

The subsurface at the gasworks site is extensively contaminated by phenols, PAH and BTEX. The BTEX contamination was caused by refuelling loss during gasworks operation time. The maximum BTEX concentrations in the loam were analysed at 2.9 g/kg. Pump-and-treat systems have been installed at the site, which may influenced the spatial distribution of SCAP.

7.1.2 Sampling

Sampling was carried out twice at this site (November 2001 and January 2002) and samples are derived from pumped water. Samples were filled into 100 mL Duran glass bottles, 100 mg $CuSO_4$ added, the top sealed with an aluminium foil cap and a screw bottle cap tightly screwed on top. The samples were then frozen and kept at –18°C until analysis was carried out. The bottles were only filled half and stored lying in the freezer to avoid bottle bursting.

7.1.3 SCAP distribution and discussion

SCAP contamination was found near a tar pit source and along the assumed groundwater flow path (Figure 63). First sampling (11/2001) took place after an extended dry period. The highest SCAP concentration was found at the tar pit with 16,000 µg/L and a PCF of 0.28. Groundwater abstracted from an observation well 50 m down gradient of the tar pit was highly contaminated. The PCF in this well is 0.44 which indicates enrichment in C_0/C_1 SCAP relative to that of the tar pit which shows a PCF as expected of a typical tar contamination. It further has a MPR of almost 400 which indicates that oxygen is present in this well and degradation is ongoing.

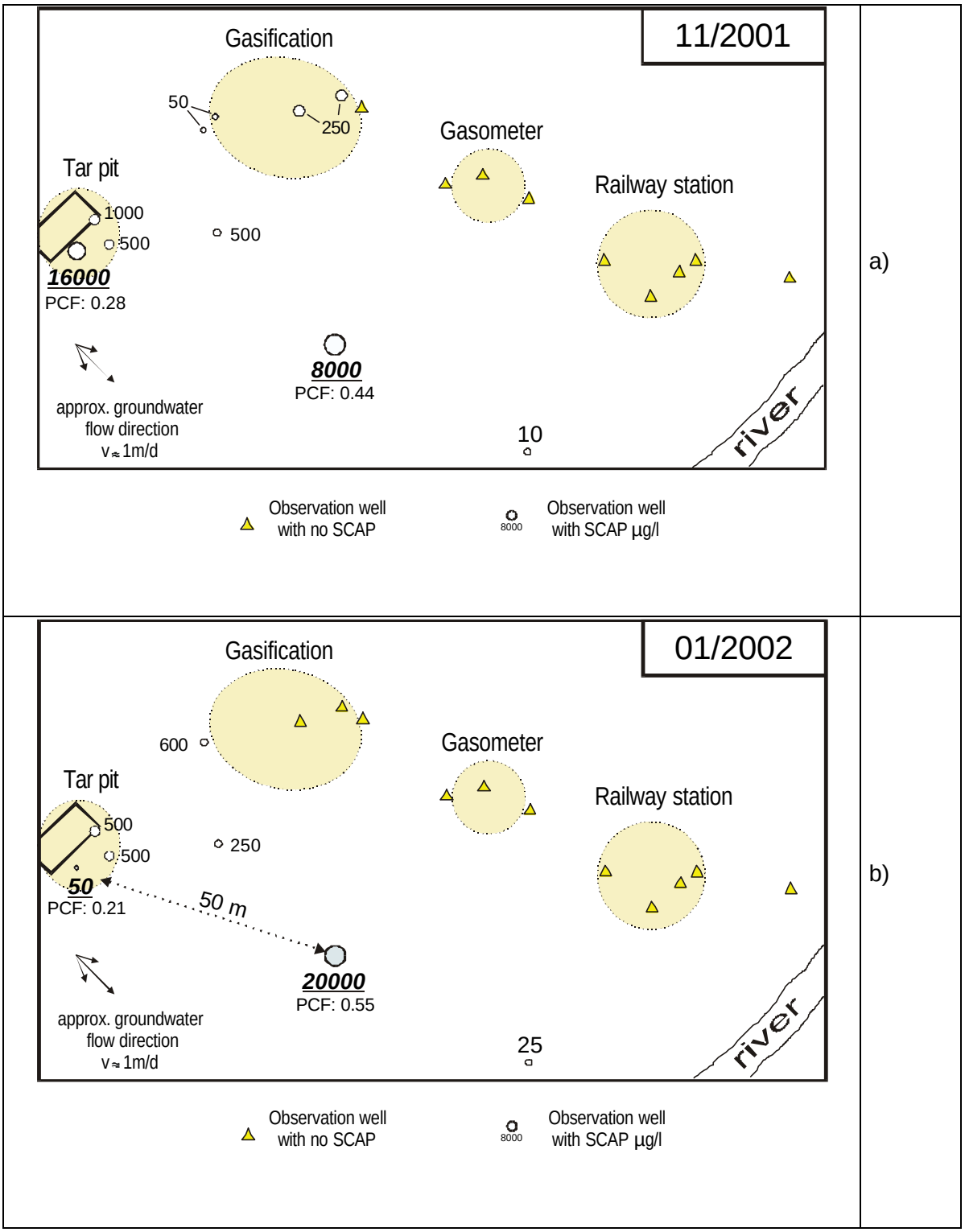


Figure 63: SCAP distribution across the gasworks site in autumn (a) and after aquifer recharge in winter (b)

The second sampling campaign (01/2002) was carried out 2 months later when numerous rainstorm events lead to significant aquifer recharge. The highest SCAP concentration was now measured at the downstream well with an even higher concentration of 20,000 µg/L than observed at the tar pit two months ago. Simultaneously, the SCAP concentration at the source well near the tar pit had dropped to only 50 µg/l which is just above 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 represents the recharge water that flushed the source 60 days earlier. The PCF at the tar pit has dropped to 0.21 within these 60 days while the PCF at the observation well increased to 0.55. The MPR has also decreased to only 6. The contaminant flow is much faster than degradation processes. This may complicate the mapping of a steady phenol plume in such aquifers. Unfortunately, there are no more wells within the assumed SCAP plume to further investigate its progress and to determine if the river water is at risk.

In sum, these findings indicate that C_0-C_1 SCAP can travel quasi non-retarded. 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.

7.2 SCAP in a tertiary sandy aquifer from a tar plant

The unpublished report of the consultant Jena GEOS is the basis for the site description. Further data were provided by Hannes & Partner (Rositz), LEG Thüringen and TLUG Jena. Although, many observation wells have been installed at this site, only very limited monitoring took place while this study was conducted. Only about 10% of all monitoring wells could be sampled.

7.2.1 Introduction to the field site

The next section describes and discusses some aspects of the geological and hydrogeological settings in the vicinity of Rositz. The geology is rather complicated and influenced by open cast and deep mining. A comprehensive overview can be found in KOLDITZ (2002) and MÜLLER (2002). A simplified overview is given in Tab. 21.

Without prominent marker horizons, the Quaternary strata classification is rather difficult. Quaternary deposits such as Pleistocene terrace gravel or glacifluviatile deposits do not form extensive aquifers and are only of local importance. Often these sandy or gravel layers are unsaturated. Nonetheless, they can be relevant for the transport of pollutants via hydraulic connections to the more important Tertiary aquifers below (KELLER *et al.* (1992)).

Tab. 21: Quaternary and Tertiary geology and hydrogeology in the vicinity of Rositz

Strata	**Average Thickness**	
Holocene	0,3 – 0,4 m	**Quaternery**
Aquifer 11	no details possible	
Ground moraine of the Saale-glacial period	4 m	
Aquifer 15, 17	no details possible	
Ground moraine of the Elster-glacial period	2 m	
Aquifer 2, i.e. aquifer 28	no details possible	
Seam 4	6,5 (with aquifer 282)	**Tertiary**
Aquifer 3	4 m	
Seam 23	about 11 m	
Aquifer 4	about 7 m	
Seam 23	about 11 m	
Aquifer 5/6, i.e. aquifer 52	about 17 m	
Seam 1, separates aquifer 5 and 6	5 m	
Pretertiary (Triassic, *Zechstein* rocks)		

The limnic *Luckenau clay complex* together with the *Thuringian-Saxonian Seam* (Seam 23) lie above **aquifer 5** and and represent an aquitard. The grey to grey brown coloured clays beneath the seam have a thickness of 0.4 m to 6.8 m.

The **Thuringian- Saxonian Lower Seam** (Seam 1) is only occasionally present. With this aquitard missing the **aquifers 5 and 6** are connected and can therefore be treated as a single unit which represents the main local aquifer system. The aquifer system is very inhomogeneous and consists of the fluvial deposits from the tertiary Altenburg river system. In most cases the aquifer is constituated of fine to medium gravels and/or medium to coarse sands (90 % (wt/wt) quartz pebbles, KUHN (1998)). Locally, it also appears in form of very thin clayey, silty and coarse gravely layers. Gutter-like structures are of great importance to the groundwater flow behaviour in the adjacent area to Rositz as published by HÄNEL, THÜRINGER GEOLOGISCHER VEREIN E.V. (1998) or WUCHER *et al.* (1994). Thickness as well as transmissivity increase from south-east to north-west and thus mark the former flow of the Altenburg river (STEINMÜLLER (1995)). The grain size decreases significantly from the lower (5/6) to the upper aquifers (4 and 3).

The hydrogeological conditions observed today are seriously effected by the extensive opencast and deep mining which took place in this region until the 20 (th) century. Mainly, the underlying and overlying sediments of Seam 23 were destroyed and have only occasionally been back-filled. Stratification disruptions in the underlying beds often occurs in areas where underground mining was carried out. This mining of aquitards has lead to some hydraulic contacts between different aquifers with the consequence of extensive

pollution in all aquifers.

The former opencast mine “Neue Sorge” resulted in a pit of 16 – 18 m depth, not deep enough to touch the aquifer 52. Today this mining pit is filled with tar residuals. It is not confirmed but suspected that the “Neue Sorge” contributes to the high pollutant concentrations found north of the tar processing plant. It is currently discussed that the tar residues consolidate at the bottom of such lakes, forming an impermeable base (POETKE (2001)).

7.2.2 Sampling

Sampling was carried out twice at this site. The plume downgradient to the site was sampled in July 2000 (109/91, 121/92, 311/92, 408/94– displayed in italic letters) and the wells at the factory premises were sampled in June 2002. All samples are derived from pumped water from the aquifer 52. Samples were filled into 100 mL Duran glass bottles, 100 mg $CuSO_4$ added, the top sealed with an aluminium foil cap and a screw bottle cap tightly screwed on top. The samples were then frozen and kept at –18°C until analysis was carried out. The bottles were only filled half and stored lying in the freezer to avoid bottle bursting.

7.2.3 SCAP Distribution

The SCAP distribution, its concentration and the PCF across the site and its downgradient plume are summarised in Tab. 22.

Tab. 22: Concentration and PCF observed at sampled observation wells (Full data in Apendix)

Name	SCAP µg/L	PCF	Name	SCAP µg/L	PCF
102/91	20.8	0.00	306/92	10100	0.60
105/92	30.6	0.88	307/92	4.61	0.00
109/91	*48.6*	*0.00*	*311/92*	*127*	*0.00*
121/92	*827*	*0.00*	408/94	0.00	0.00
203/92	0.50	0.00	BK84	0.00	0.00
304/92	4200	0.02	7/94	4010	0.21

From the few data it is rather difficult to derive some final analysis for this field site. Nonetheless, an attempt is made. By looking closely at the points displayed in the map in Figure 64 and Figure 65 it becomes apparent, that SCAP move along with the preferential

groundwater flow. The downstream wells 311/92 and 121/92 are SCAP contaminated and lay within the predicted plume within aquifer 52. The plume may easily be 2 km in length and corresponds to a travel time of 50 years. The earlier supported statement that the contaminated groundwater sinks into the *Plattendolomit* at the factory premises and then rises up again into the tertiary aquifers (5/6) further north (WUCHER *et al.* (1994)) can based on the zero PCF observed at 121/92 not be supported. This zero PCF value indicates that degradation processes must have occurred along the flow path to this observation well but further studies within the same *Zechstein* formation at Deuben and Profen showed no evidence for a degradation potential of those deeply buried aquifer systems. In fact, such deep aquifers show an increased PCF at the tip of the plume. Therefore, if SCAP would sink into the *Plattendolomit* and would rise up again further north must lead to a PCF > 0 should be observable in the downstream wells.

The observation well 408/94, which is placed inside the aquifer 6, is as expected uncontaminated. The SCAP plume must divert into north west western direction once the aquifer 52 meets the aquifer 6 due to the water velocity expected with the extensive aquifer 6.

The tar lakes may not directly recharge to the Tertiary aquifers either due to a consolidated basement of the lakes or that they are not excavated into this aquifer. If no hydraulic windows are present close by and the protecting clay layer and/or coal seam above the aquifer 52 are still present the tar lakes will not directly contribute to the contamination in aquifer 52.

From the few data collected at only one sampling event on the site the following interpretation can be derived. It is possible to clearly distinguish between contaminated and uncontaminated wells. It is also possible to identify the geologically predicted hydraulic connections at the site (WUCHER *et al.* (1994)) by the SCAP data.

A PCF of 0.21 at the observation well 7/94 may indicate that this well is close to a hydraulic connection between the Quaternary and the Tertiary aquifer (=hydraulic window) where tar contaminated water recharges the aquifer. In fact, a tar pit is close to the hydraulic window in that area as postulated by KOLDITZ (2002) as shown in Figure 66.

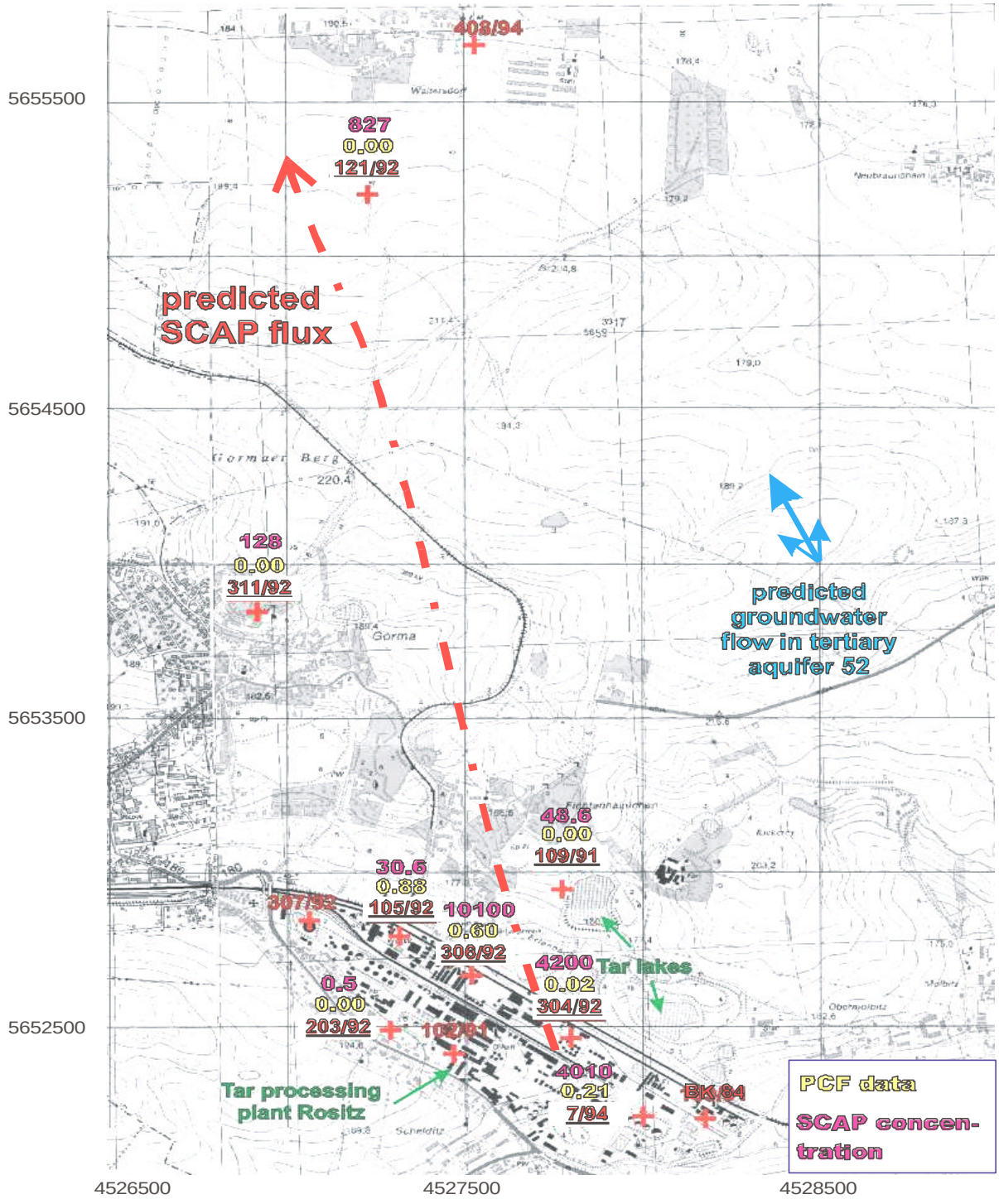


Figure 64: SCAP distribution across the site, underlined well contain SCAP

The contaminated well 306/92 has a PCF of 0.6 and displays with more than 10 mg/L the highest concentration observed at the site. The PCF most likely indicates that this well is downgradient of the contamination found in 7/94. Inorganic compounds such as sodium and chloride as shown in Tab. 23 support this hypothesis. The highest salt concentration observed at the site corresponds well with the highest SCAP concentration that has an increased PCF relative to the source.

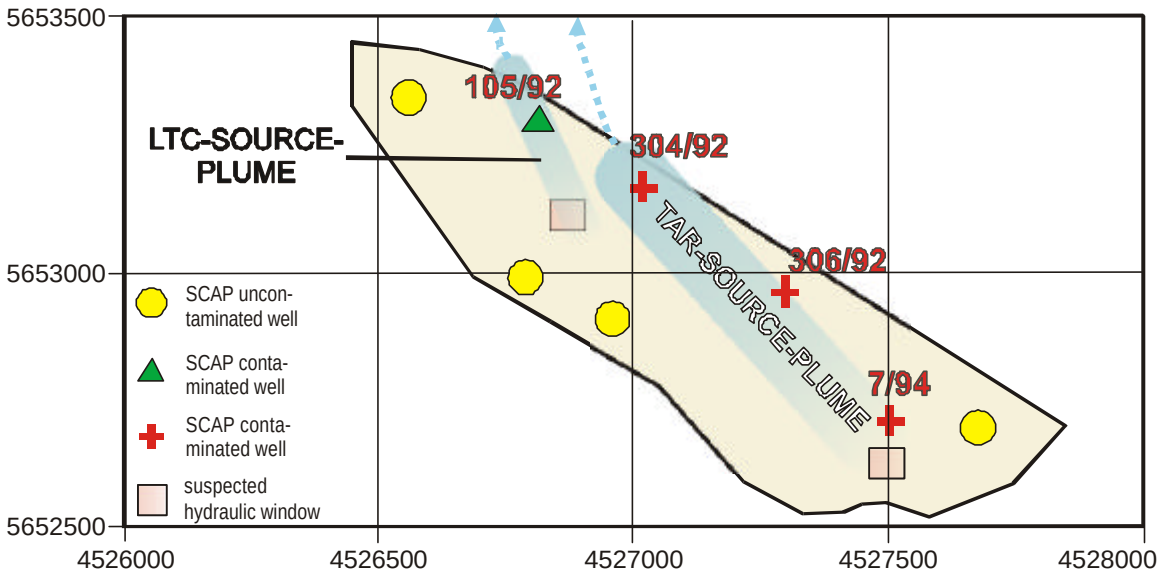


Figure 65: Sketch of predicted SCAP plumes at the tar processing plant premises

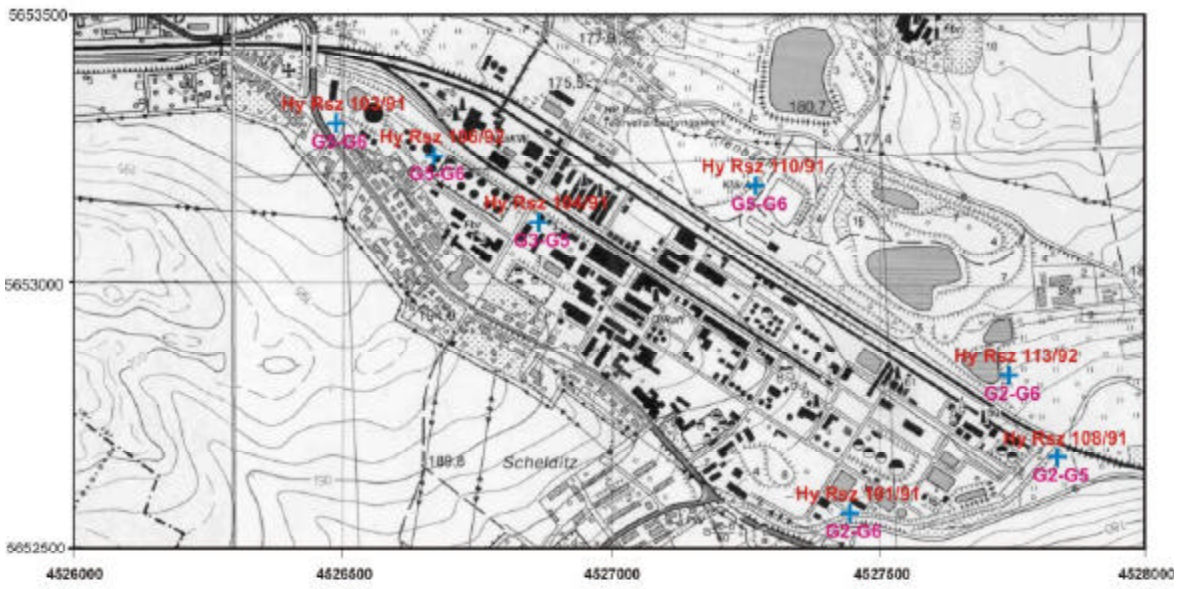


Figure 66: mapped hydraulic windows at the plant premises (KOLDITZ (2002))

The observed PCF of 0.02 at 304/92 with its concentration of 4 mg/L would then indicate the tip of the plume since as stated earlier such a low PCF can only be a result of degradation processes. This well showed an elevated temperature of more than 2°C above site average which could indicate degradation processes occurring. Unfortunately, no redox potential measurements were carried out during sampling. However, with low salt concentrations it is very likely that OW 306/92 represents the fringe of the plume.

Tab. 23: Inorganic data from water analysis at three wells within one plume (June 2002)

concentration in mg/l	7/94 (source)	304/92 (plume)	306/92 (fringe)
Potassium	262	291	223
Sodium	56.3	324	131
Chloride	61.0	102	100
Sulphate	390	270	140
Calcium	8.8	8.3	7.3
Magnesium	42.5	59.1	46
Bicarbonate	634	1600	923
Ammonia	1.8	10.4	2.5
Nitrate	0.9	2.0	1.1

The observation well 105/92 north-west of well 306/92 has a very low concentration (30 µg/L) with a very high PCF of 0.88. This could indicate that this well is contaminated by a source different from that of the other wells on the site. The contamination observed may be caused by LTC waters which could have been produced from the power plant surrounding the well. In sum, that yields a very narrow plume leaving the site in north-western direction and crossing the premise's border within its north-western third.

7.3 Deep injection of LTC water in a carbonate aquifer

The LTC plants Profen and Deuben of the A. Riebeck'schen Montan Werke AG began in 1936 with the extraction of tar, light oil and LTC coke by the Lurgi-LTC from subbituminous coal or its briquettes in the Zeitz-Weißenfels mining area. After 1949 the LTC plants continued their production within the VEB Braunkohlewerk „Erich Weinert" which has been closed down in the early 1990's. According to STRUZINA (1997) brown coal briquettes were carbonised by the Lurgi-process in the LTC plant Deuben. There is no information on the carbonisation process for the LTC plant Profen, but the Lurgi-process may have been applied here too. Within a period of approximately 30 years around 8 million m³ of waste water were injected, which corresponds to a total mass of approximately 120,000 t phenol (Figure 67). There are significant differences between the two sites in relation to their operation time and their quantity of waste water injected.

Five injection wells in Profen and six injection wells in Deuben/Trebnitz were drilled into the reef limestone and into the *Zechstein-Plattendolomit* until 1944 (see map Figure 68). The borehole diameter at the *Zechstein* horizon was 165 – 216 mm. The areas above the *Zechstein* were cased off while the injection sections were completed as open hole.

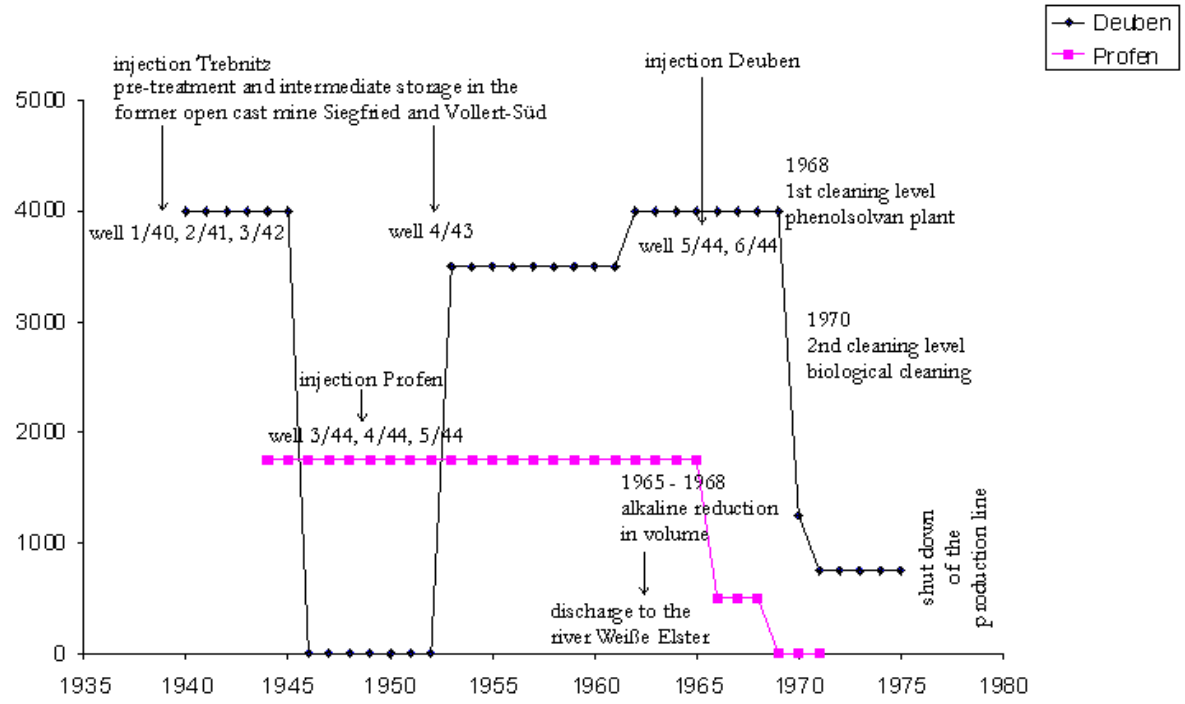


Figure 67: Injection scheme for the two sites (translated from REHBERG (2002))

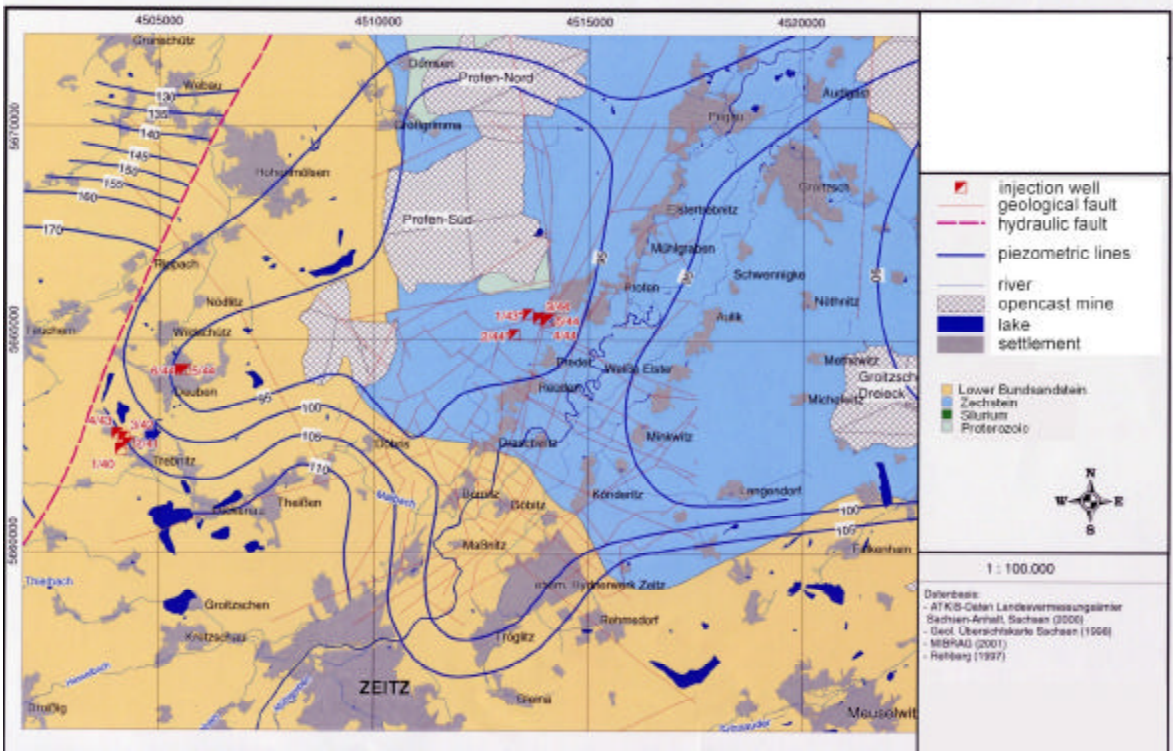


Figure 68: Geological /hydrogeological map with injection wells and piezometric surface in the *Zechstein* aquifers as proposed by REHBERG (2002)

In 2001, six wells (3 at both sites) were drilled by the Umweltforschungszentrum (UFZ) to investigate the present state of the contamination at the 2 sites.

Sampling: Based on own previously conducted experiments the following sample procedure was applied. Once every meter within the *Zechstein* formation a piece of core material (about 100-150 g) was removed with a clean tongs and immediately immersed into liquid nitrogen for about 15 seconds. This shock frozen piece is then wrapped into clean aluminium foil and placed into an argon filled gas tight bag and tightly sealed. Those bags were stored at –18°C until the samples were further prepared.

Sample preparation: The frozen samples were treated individually. In the frozen state the samples were divided into smaller pieces with a hammer and chisel. Those smaller pieces were than placed into a cooled clean ball mill together with 3 small pieces of dry ice. The dry ice kept the temperature low during grinding and covered the sample with a carbon dioxide atmosphere. The ground sample was placed into clean aluminium foil and together with a small piece of dry ice into a gas tight bag. It was then stored until extraction at –18°C. This work procedure needed to be followed, since the samples were grind in Jena, but extraction and analysis was only possible at the UFZ in Halle.

Sample extraction and extract analysis: The samples were extracted by the author following the method as described in chapter 4.3.3. The analysis of the extracts was carried out by the author with the method developed for aqueous samples (chapter 4.3).

In total, about 100 solid samples were prepared, extracted in duplicate and analysed in triplicate which amounts to 600 analyses in total. Together with blanks, standards and dilutions around 700 analyses were performed.

Water samples were taken within 6-8 week intervals between summer 2001 and summer 2002. Unfortunately, the samples were bailed and not pumped. Due to the depth of the contamination, the bailing lead to rather dilute samples as the inorganic data from the latest pumped samples showed. Although water samples were analysed for SCAP those data will not be presented in this study. SCAP data in water samples however, are included in a more general report on those 2 sites (REHBERG (2002)).

7.3.1 Profen

With permission of the Prussian mining authority in Zeitz the LTC plant Profen began the injection of LTC waters at the end of 1944 into the wells 3/44 and 4/44. Later, the injection was continued into well 5/44. The wells 1/43 and 2/44 were not used for injection due to their low hydraulic conductivity. The waste water quantities injected amount to approximately 100-150 m^3 per day. From 1965 to 1968 the waste waters were cleaned by alkaline treatment, reduced in volume and discharged into the river Weiße Elster (HUTH (1972)). From 1969 to January 1971 (time of closing down) the waste waters were

transported in tank wagons to Deuben, cleaned up there (alkaline treatment) and the treated water injected into the wells 5/44 and 6/44.

Three boreholes (UFZ 101, UFZ 201 and UFZ 301 short: UFZ 1, UFZ 2, UFZ 3) were drilled in 2001 to investigate the phenol contamination together with the geology of the site Profen.

7.3.1.1 Geology and Hydrogeology

The boreholes show the injection horizon, a *Zechstein* reef as well as its lateral facies representations. Below the reef a dense greyish green, shale siltstone is developed. It is assigned to the bedrock and is of Ordovician to early Palaeozoic age. Its joints are almost completely filled with calcite or hematite. The top of the bedrock was found to be at –51 m AOD (UFZ 101), -60.11 m AOD (UFZ 201) and –47.9 m AOD (UFZ 301). It dips westwards. It has a low porosity (~4%) and works as an aquitard.

It is followed by a porous Bryozoa reef, which is highly suspected to be the injection horizon. The reef has a maximum thickness of 110 m. The transitional stratification between basement and reef is about 1.5 – 5 m in thickness and rather differently developed. In borehole UFZ 101 it is an alteration of dolomite and limestone fragments with shale fragments, in borehole UFZ 301 a dark grey claystone with thin layers of gypsum and pyrite. Data on UFZ 201 are missing.

The *Zechstein* surface in UFZ 101 lies at 63.96 m AOD, in UFZ 201 at –49.11 m AOD and in UFZ 301 at 13.5 m AOD. There is no fundamental evidence on why the *Zechstein* surface should be at 13.5 m AOD in UFZ 301. It is even more likely that this surface will occur at approximately –30 m AOD, since a compact dolomite structure occurs at this point. Just above this structure a collapsed formation is described, which cannot be assigned to a single stratigraphic unit. The reef surface, which is postulated to be this dolomite structure, dips steeply into NW and slightly from SSW to NNE. The facts, that the bedrock was found at different depths in UFZ 101 and UFZ 201 and that the reef surface in Profen 1/43 is at –50 m NN confirm the existence of a geological fault in the bedrock as well as in the *Zechstein* formation.

Karstified limestones are found at the top of UFZ 101 with increasing dolomitisation with depth. The high porosity of the dolomites decreases with depth from 24.5% at 45.5 m AOD to 19,3% at –4.3 m AOD. A decrease in the number of joints can also be noticed. The proportion of biogenic material (shells, Bryozoa, corals) is very high. In the pores and at the fracture surfaces greyish to black coatings with noticeable smell are found. Calcite, dolomite and pyrite precipitates at these surfaces have been described by REHBERG (2002).

The *Zechstein* in UFZ 201 occurs as a very hard, dense dolomite with a thickness of 11 m only. It contains single thin clay layers of up to 5 mm thickness. Compared to UFZ 101 the proportion of biogenic material is rather low. The dolomite has a porosity of around 0.2 – 6.3% only. Just a few open joints have been described.

A 16.4 m thick limestone associated in a collapsed structural formation with a high clay content has been reported in the top of borehole UFZ 301. It is followed by a 20.5 m thick complex of clay and little consolidated chalky clay-/siltstones and fine sandstones. They were probably deposited during a period of reef destruction. Below, a 22 m thick dolomite structure is found, which contains ca. 17 m of cellular-porous dolomite. The proportion of biogenic material is again high. There are indications of intensively jointed horizons at – 38.9 m AOD (loss of core area). At its base the dolomite changes into a dense dolomitic claystone.

Within the last 50 years the operation of open cast mines and extensive waterworks in this region induced a decline of the confined water table in the *Zechstein* aquifer from 127.5 m AOD (1944) to about 97 m AOD (2002). This results in a decrease of about 30.5 m. In spite of variations caused by atmospheric pressure during the period of water level recording (12.05.01-28.03.02) a steady rise of the water table could be observed. On 22./23.07.2002 the water table lies at 96.82 m AOD (UFZ 101), 96.83 m AOD (UFZ 201) and 96.76 m AOD (UFZ 301) (Figure 69). The unusual behaviour of the water table in the UFZ 201 represents nothing but the declining curve of the slug test carried several months earlier. This emphasises the fact that the *Plattendolomit* in UFZ 201 is of very dense nature and there is only very limited groundwater flow to the *Zechstein* formation in borehole UFZ 201. The few open joints bear some groundwater and thus no hydraulic contacts to the water bearing parts of the reef in the SE exist.

The water table fluctuations are identical in the boreholes UFZ 101 and UFZ 301. This may be due to a similar connection to the Tertiary sediments. They may also well be connected to each other.

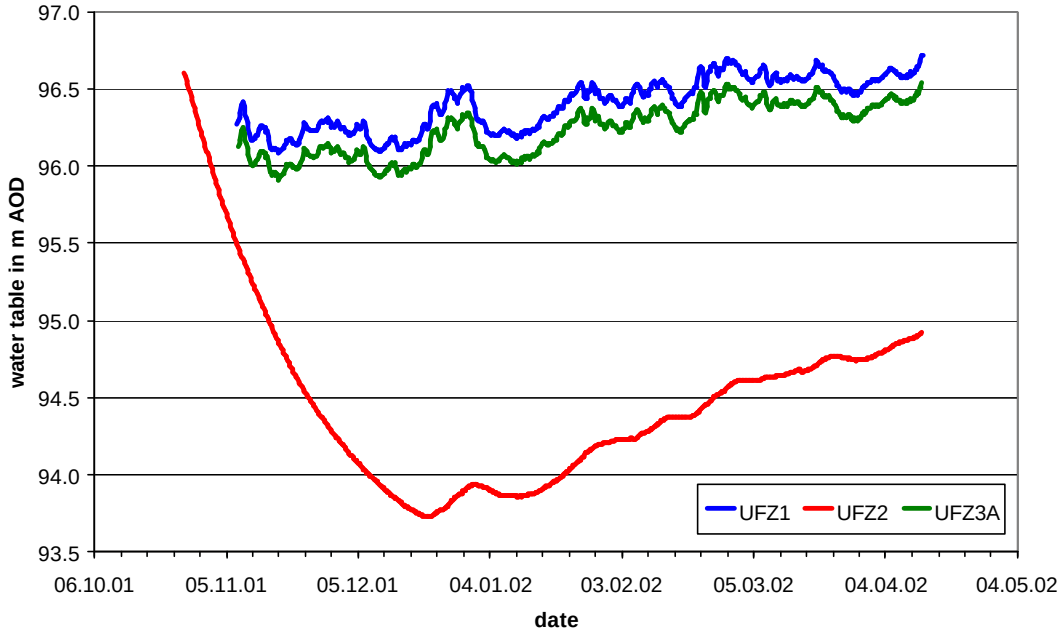


Figure 69: Watertable fluctuation in the *Zechstein* formation at Profen recorded with a pressure transducer

7.3.1.2 SCAP distribution and interpretation

A SCAP contamination was found only in UFZ 101 and UFZ 301 at this site. Those two wells are shown together with their lithology in Figure 70. The well UFZ 202 was uncontaminated mainly due to its dense formation and is not displayed. Unfortunately, the first cores prepared and provided for analysis by the samplers onsite for UFZ 101 and UFZ 301 already contained SCAP. Thus, nothing can be said about the point at which the contamination exactly starts at. Although the broyoza reef is more than 100 m in thickness, only the upper half has been sampled for SCAP analysis. There were still SCAP present in the core sample extract at the point were no more drilling cores were prepared and provided for analysis. For this reason, it can not clearly be stated, that the reef is uncontaminated blow -6 m AOD.

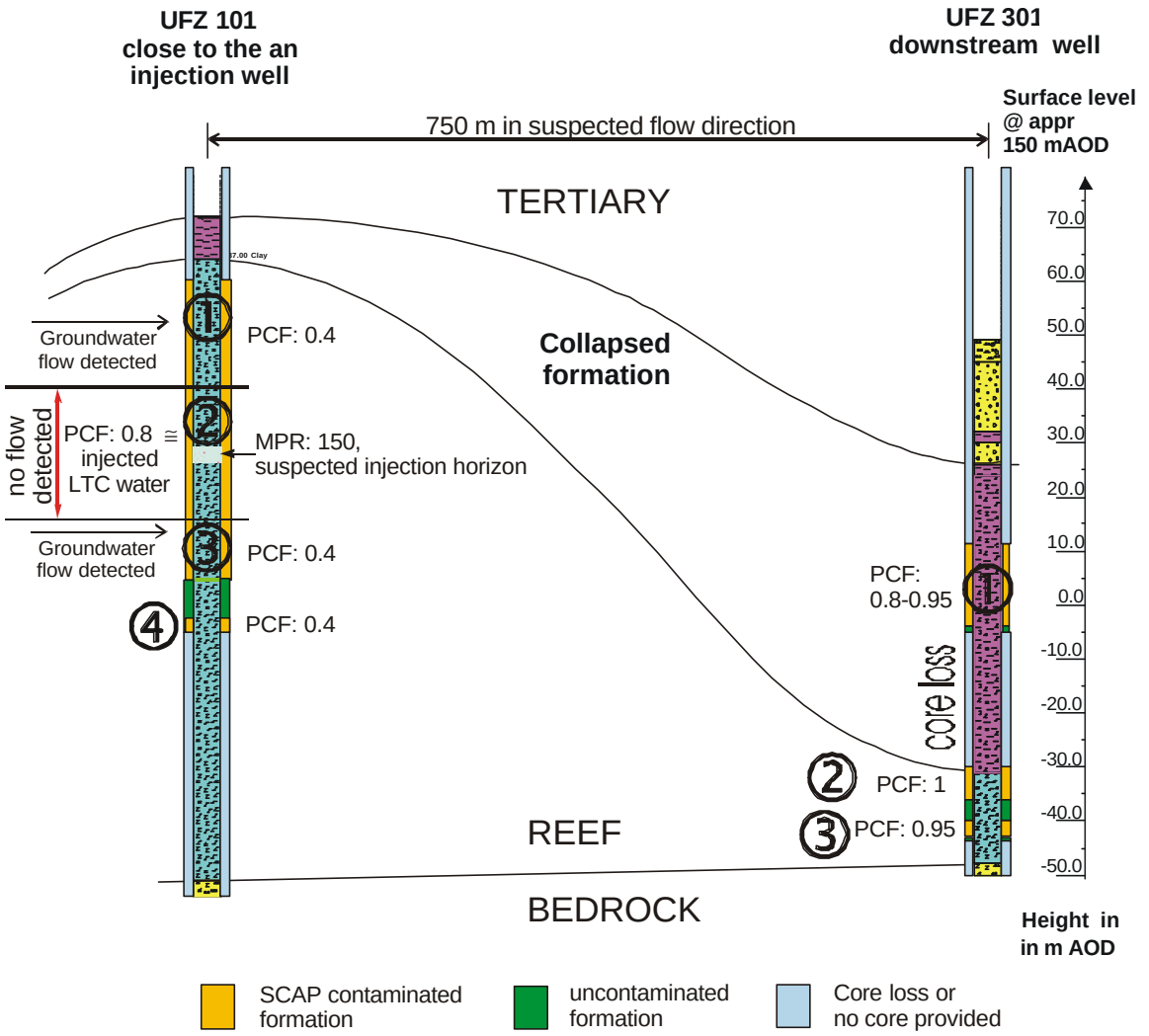


Figure 70: SCAP contamination together with the geological setting at Profen

UFZ 101 is the well closed to the former injection well nest 1/43, 2/44-5/44. It is suspected that it still represents the conditions present today in the source wells. Although the contamination is only split into two sections (60 m to 1 m AOD and –4 m to –6 m AOD), the first section must be further split (Figure 70). The SCAP contamination in the downstream well **UFZ 301** can be divided into 3 individual sections (Figure 70). Those may represent 3 individual flow paths. Section ① starts at 11 m AOD (137 m bgl). Section ② lays below the section of coreloss at -30 m AOD (179 m bgl) and section ③ can be found between -40 m and –42 m AOD (189 m bgl – 191 m bgl).

In the following chapter the SCAP distribution in the core samples at UFZ 101 will be discussed in greater detail. The assumed injection horizon at 123 m bgl (28 m AOD) is still visible today which indicates that the contamination did not get washed out. An MPR of 150 at this depth clearly indicates, that oxygen containing water must have reached this depth. As illustrated in Figure 71, the MPR peaks very sharply at this horizon. The LTC waters at Profen were not directly injected but transported several miles in pipelines and channels to a reservoir thus the water had time to get enriched in oxygen and phenol and

p-cresol degradation processes may already have been induced above ground before injection.

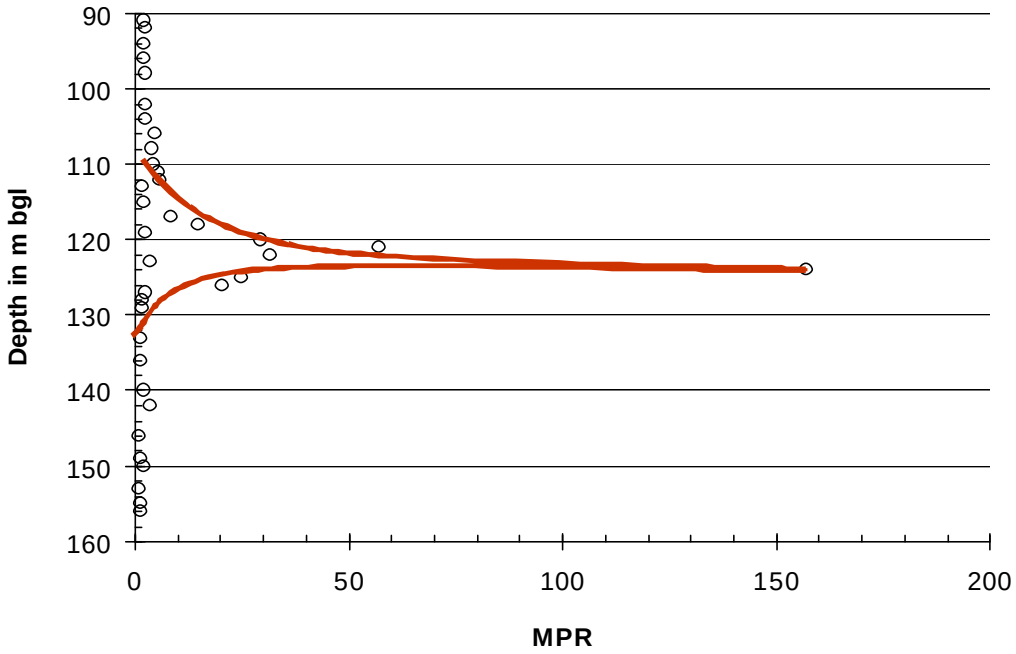


Figure 71: MPR data within the core samples from UFZ 101

With the MPR indicating degradation, the PCF data can not be taken without correction. They have been corrected in the following way. It is assumed that the ratio of para to meta cresol does not change and the phenol concentration is constant with respect to all other SCAP. This correction greatly reduces the noise in the PCF and brings it to an almost constant value of 0.8 within the depth of 111 m bgl and 131 m bgl (40 m – 20 m AOD) (Figure 72). This PCF value of 0.8 is similar if not identical to the PCF of the injected water. LTC water typically has a PCF of 0.8 (GUNDERMANN (1964), V. ALBERTI (1983)).

Above and below section ② in UFZ 101 lay the sections ① and ③ in which the PCF value has decreased to 0.4. A decreasing PCF can only be observed if the easier soluble SCAP fractions get washed out over time. This requirement is fulfilled since groundwater flow has been shown to occur within the two sections.

Section ② in UFZ 101 lays in a very uniformly formation which is characterised by a low clay content (Figure 72) and an effective porosity of 0.15-0.2. From those data one should expect a highly conductive horizon. But SCAP data and flow meter measurements in the open borehole showed that this section seems to be hydraulically inactive. This corresponds to the high PCF value found as well as with this MPR signature still present today after more than 30 years past closure. It may however have some joints and fractures.

The same pattern is again demonstrated in Figure 73, which displays a corrected PCF together with the total SCAP concentration for the core samples in UFZ 101. The highest SCAP concentrations within the analysed core samples are found just above section ② (point A in Figure 73), at the suspected injection depth and just below section ② (point B in Figure 73). At point A, the high SCAP concentration (8.8 mg/kg) is related to a low PCF (0.48) while at point B the high SCAP concentration (10.3 mg/kg) is related to a high PCF (0.8). This may indicate, that preferential contaminant flow occurred in section ①. Point A coincides with the lowest clay content observed within this section, indicating excellent hydraulic conditions. The highest concentration found at point B does unfortunately not correlate as well with the clay content. It could however indicate the presence of a horizon with a low effective porosity at 133 m bgl (18 m AOD).

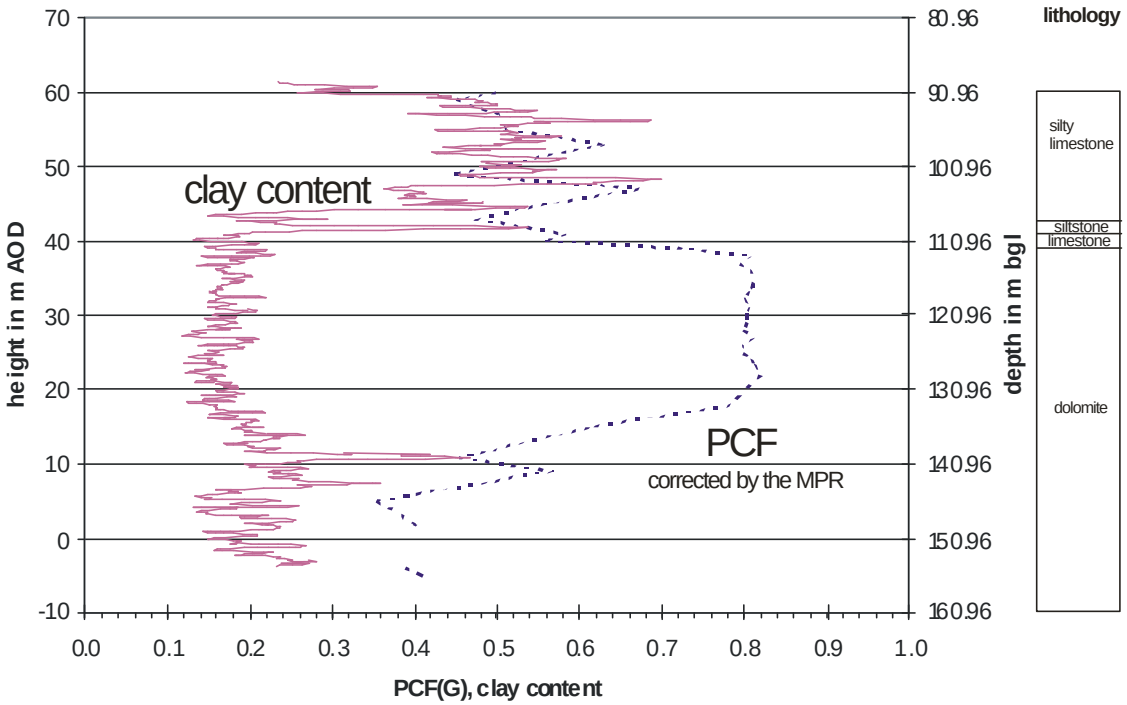


Figure 72: Clay content in UFZ 101, corrected by inorganic data[29]

[29] Clay concent curve provided by Dr. H. Gläser, UFZ Halle, core samples for inorganic analysis were prepared according to DIN 38414/7 (S7) digestion method.

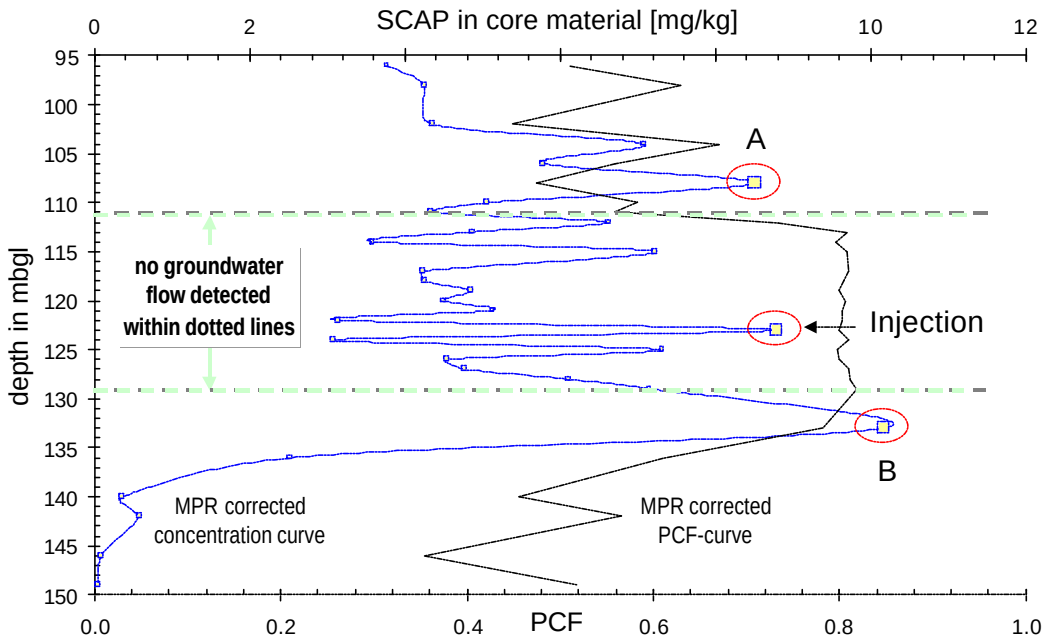


Figure 73: Depth profile of corrected PCF and corrected total SCAP concentration UFZ 101

The situation in the downgradient well **UFZ 301** can be interpreted as follows. Generally, the following principles apply. A higher PCF can be observed with:

a) increasing travel distance
b) increasing adsorption capacity of the aquifer material
c) deacreasing flow velocity, increased contact time

If adsorption capacity and water velocity are minimised in their influence due to the nature of the aquifer than the length of the flow path becomes dominant.

Section ① in UFZ 301, starting at 11 m AOD (137 m bgl), is characterised by a PCF of 0.8 to 0.95 with a steady rise in PCF with depth (Figure 74). The upper part of section ① can be found at the same depth as section ③ and ④ from UFZ 101. This may indicate a rather horizontal contaminant flow from UFZ 101 to UFZ 301. The other 2 sections in UFZ 301 have PCF values of at least 0.95 which could be the result of a longer SCAP flow path. At –38.9 m AOD extensive joints were detected by borehole logging and those correspond very well with the highest PCF observed in this well.

However, a general correlation between the contamination in UFZ 101 and UFZ 301 can not be given. This is mainly due to the complex geological structure existing within such reef systems which cannot be investigated by only 2 boreholes. Further investigations need to be carried out.

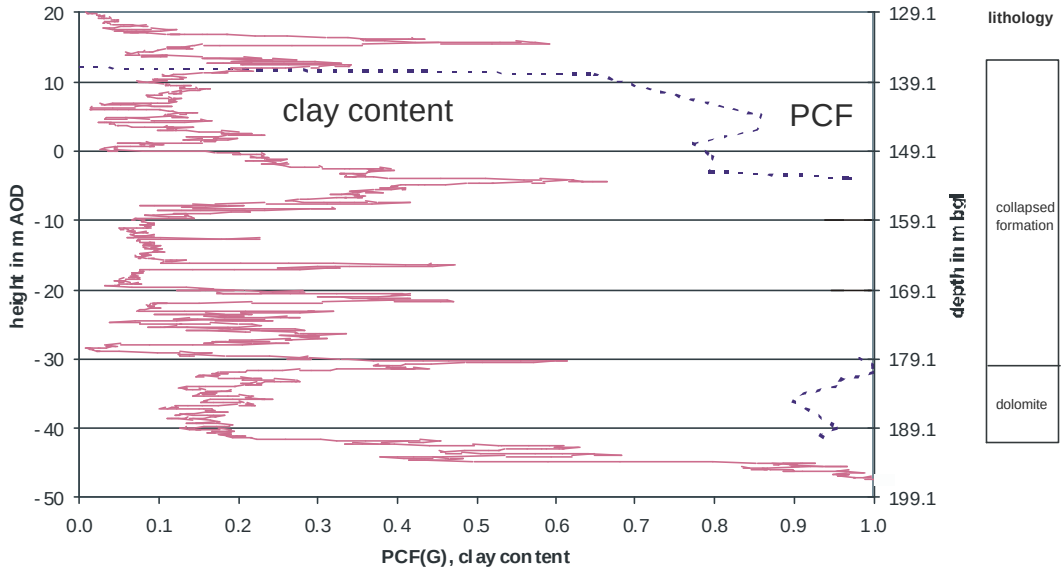


Figure 74: Clay content in UFZ 301, corrected by inorganic data

7.3.2 Deuben

With permission of the Oberbergamt Halle the LTC plant Deuben began around 1939/40 with the injection of phenolic waste waters in the subsoil. The waste water quantities in Deuben reached up to 450 m³ per day. Until 1961 the LTC waters were discharged into the former open cast mine Siegfried respectively Vollert-Süd for an intermediate storage and pre-treatment (ECCARIUS (2000)) and then injected into the four deep wells in Trebnitz.

The injection capacity of the wells decreased with time and some wells had to be abandoned. The wells 1/40, 2/41 and 3/42 at the site in Trebnitz reached their maximum injectable amount already in 1955. In 1959 the injection capacity of the well 4/44 was very restricted so that the LTC waters were injected with a pressure of 4 at (58 psi, 405 kPa). From 1961 to 1975 (time of closing down) waters were injected directly into the wells 5/44 and 6/44.

The introduction of a waste water treatment by the phenolsolvan process strongly reduced the SCAP concentrations from 10 – 12 g/l in the beginning to 1 – 2 g/l (data are *phenolindex* meassurements). The first phenolsolvan plant was completed by 1945 (v. ALBERTI (1983)), however removed by the Soviet Union as war reparation. A new phenolsolvan plant in Deuben did not start operation until 1968 (HUTH (1972); PLÖTTNER (1997)). This water treatment was accomplished in 1970 with a biological treatment.

7.3.2.1 Geology and Hydrogeology

At this site boreholes UFZ 401, UFZ 501 and UFZ 601 have been drilled. The injection horizon is developed in bedded facies as the so-called *Plattendolomit*. Below the *Plattendolomit* lies a grey clay with fragments of dolomite, clay- and siltstone known as Grauer Salzton. Its top can be found at 77.72 m AOD (UFZ 401), 61.18 m AOD (UFZ 501) and –2.01 m NN (UFZ 601). The displacement of about 63 m between UFZ 501 and UFZ 601 is caused by a fault and leaching processes (REHBERG (2002)).

The mainly dense *Plattendolomit* in **UFZ 401** reaches a thickness of 19 m. It is characterised by many joints. At its top clayey to silty, partly sandy strata of the *Upper Letten* and the *Lower Buntsandstein* follow. The *Plattendolomit* of the **UFZ 501** has a thickness of 24 m. It is a grey to dark grey, platy to bedded, fine crystalline dolomite. It has narrow, open joints. Single joints have dark grey to black coatings. Clayey to silty sediments of the *Upper Letten* and the weathered *Lower Buntsandstein* are at the top with a thickness of 10 m. In **UFZ 601** the *Plattendolomit* reaches a thickness of 9 m only. The so-called collapsed formation is found above the *Plattendolomit*. A local steep subsidence structure (subrosion depression) has developed between UFZ 501 and UFZ 601. It is filled with material (up to 80 m – UFZ 601) of the collapsed formation. This material consists of tertiary clays, sands, quartz gravel, clay- and siltstones, oolitic limestones of the *Lower Buntsandstein* and single fragments of dolomite of the *Zechstein*.

Within last 50 years the operation of open cast mines and large waterworks in this region induced a decline of the confined water table in the *Zechstein* aquifer in the area of Deuben/Trebnitz. The difference between 131.1 m AOD (1940) and 96.4 m AOD (2002) adds up to 34.7 m. Tab. 24 shows the latest water level measurements in the *Zechstein* aquifer:

Tab. 24: Water level in m AOD for UFZ 401-601

borehole	water level in m AOD (11.04.2002)	water level in m AOD (22./23.07.2002)
UFZ 401	99.78	100.79
UFZ 501	99.63	100.37
UFZ 601	99.54	100.55

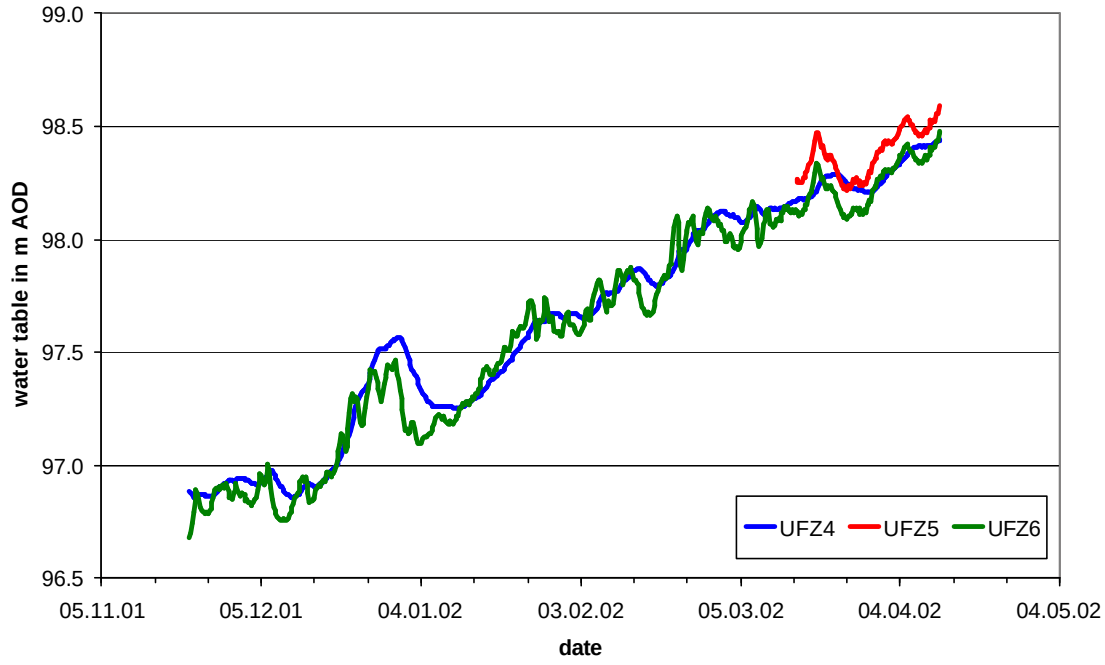


Figure 75: Watertable fluctuation in the *Zechstein* formation at Deuben recorded with a pressure transducer

Generally, the *Plattendolomit* can be described as confined and with a steadily rising water table (Figure 75). The aquifer is only slightly confined at UFZ 401 (+4 m) but increases to +15m at UFZ 501 and then to extremely confined conditions at UFZ 601 (+94 m). The possibly present subsidence structure may have hydraulicly conductive joints which could feed the *Plattendolomit*.

The water table in **UFZ 401** rose by about 2 m during the period of observation (21.11.01-28.03.02). The water table fluctuations in UFZ 401 are not as well defined as in the other two wells at the site (Figure 75). This may imply that the UFZ 401 is not well connected to the Tertiary sediments and/or the hydraulic connection to the other two wells at the site is not very effective. According to REHBERG (2002) **UFZ 501** is located downgradient of UFZ 401. SCAP distribution patterns and watertable fluctuations (Figure 75) however do not seem to confirm this. The determination of a definite groundwater flow direction is very difficult at this site. The drilled wells are not arranged in a triangular geometry and therefore do not allow the determination of the groundwater flow direction.

7.3.2.2 SCAP distribution and interpretation

SCAP contamination was found in all 3 wells as shown together with the lithology in Figure 76. Unfortunately, the first cores prepared and provided for analysis by the samplers onsite already contained SCAP. Thus, nothing can be said about the point at

which the contamination exactly starts at. From the site in Profen it was learned to provide cores also from the *Zechstein* clay (Salzton) below.

UFZ 401 and UFZ 501 are close to the former injection wells while UFZ 601 is situated in the expected downstream but influenced by a geological fault. The SCAP contamination in UFZ 401 can already be found in the *Bundsandstein* formation. Unfortunately, no sample cores from this formation has been provided for analysis by the samplers onsite from the other two wells. In all three wells the SCAP contamination is also found in the *Zechstein* clay.

As a general trend, the total SCAP concentration decreases from UFZ 401 to 601 (Figure 77) and so does the PCF. However in such a complicated geological system it is rather difficult to interpret this general trend. Therefore a closer look and interpretation will be attempted based on the PCF values.

Tab. 25: Total SCAP concentration and water content in the *Zechstein* clay at the *Plattendolomit*-clay-interface in Deuben

	water content in %	total SCAP in mg /kg
UFZ 4	10.8 %	88.6
UFZ 5	6.2 %	75.4
UFZ 6	12.3 %	28.0

An increased PCF value, relative to the injected LTC water, is found in the *Zechstein* clay in all three wells. Additionally, the clay shows the highest SCAP concentration in the 3 well profiles. This may be explained by the clay's high total porosity thus having a high water content. Since clay is rather impermeable, SCAP must have diffused into the clay. Based on diffusion it may be explained why the PCF in the *Zechstein* clay is so high relative to the respective value in the *Plattendolomit*. Generally, the smaller the organic molecule, the higher its diffusion coefficient. Phenol and cresols which are the smallest molecules among the SCAP may diffuse into the clay more easily than the other SCAP might do. Fractures within the clay further assist in the spread of SCAP into the clay. The high concentration can further be regarded as a memory effect that exists in the immobile water of the clay. To achieve such a high concentration as present today in the clay the *Plattendolomit* must have been exposed to considerably higher concentrations compared to those of today.

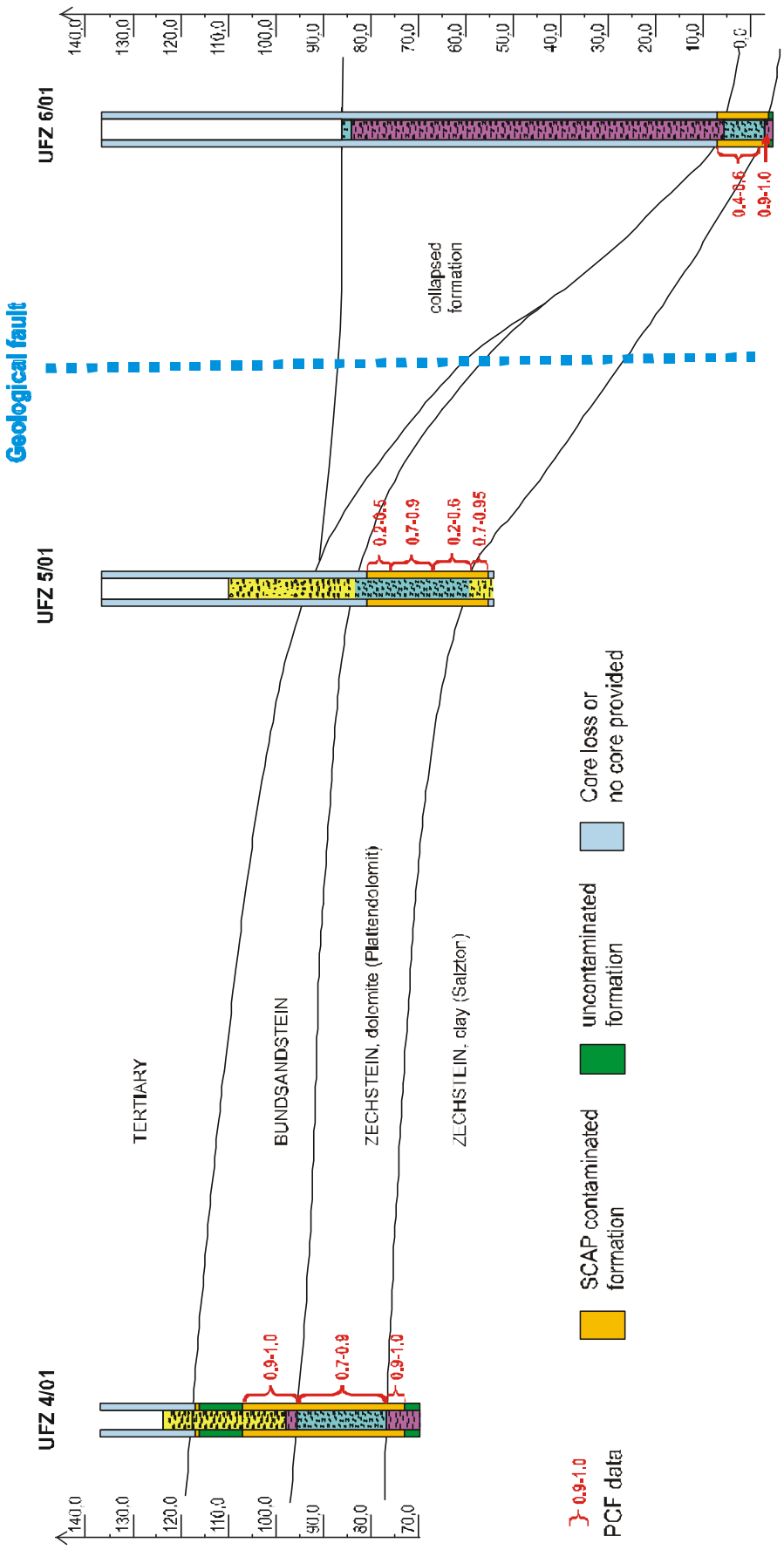


Figure 76: SCAP contamination in Deuben relative to the geological settings

The same phenomenon is observed at the *Bundsandstein-Plattendolomit*-Interface in UFZ 401 at a depth of 99 m bgl (Figure 77, Figure 78). As the clay content rises well above the average for the *Plattendolomit*, the PCF increases with it.

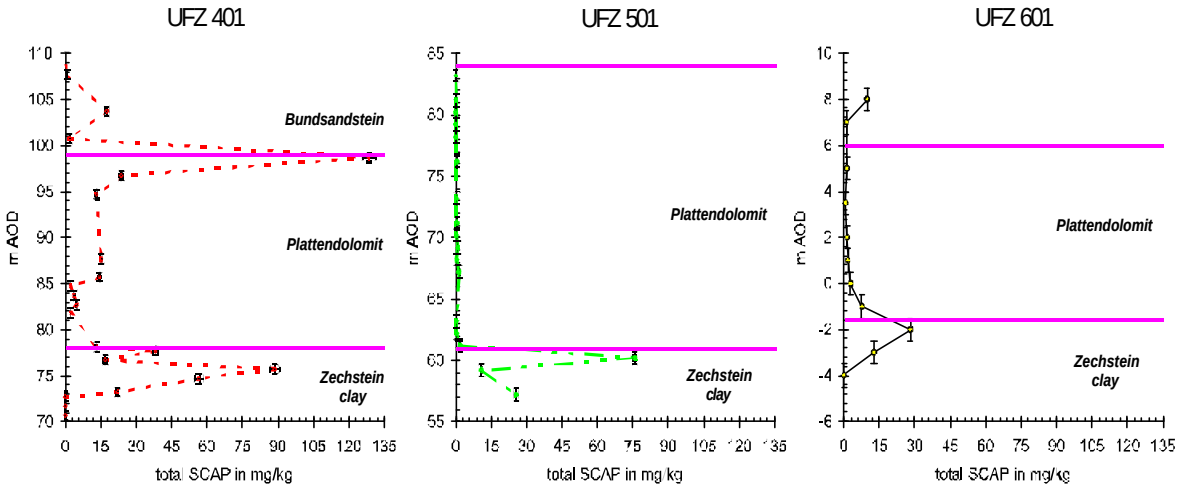


Figure 77: Total SCAP profiles in the core samples at Deuben

The PCF values within the *Plattendolomit* formation in UFZ 401 are increased relative to the injected LTC water (Figure 78). In UFZ 501 and UFZ 601, generally decreased PCF values (0.2-0.6) were determined within the *Plattendolomit* (Figure 76). MPR data, which are between 3 and 10 in all samples at the site, do not indicate similar degradation processes as in UFZ 101. This complicates the interpretation of the observed PCF data since the source wells are indicated by the PCF as downstream wells and vice versa.

A possible interpretation is presented here. At the time of operation of the injection wells, the water injected under pressure was distributed around the wells. The radius of influence of the total injected volume, calculated from an estimated total porosity of 25% and under the assumption of cylindrical and uniformly distribution around the injection well, is around 1500m in radius. That means that UFZ 601 is affected by the injection at the injection well nearest to UFZ 501. The very low gradient in the *Zechstein* water table and the fault may have helped to direct the injected water towards UFZ 601. This may explain the highly contaminated *Zechstein* clay found at the bottom of UFZ 601 as well as the high PCF within this clay. Uncontaminated water now flashes the contamination out from UFZ 601 in northward direction. It is not likely that the SCAP migrate back to UFZ 501 as the low PCF indicates in the *Plattendolomit* formation at UFZ 501. The very high PCF at UFZ 401 still comes as a surprise. However, hydraulic gradients present in June 2002 indicate a water flow from UFZ 501 to UFZ 601.

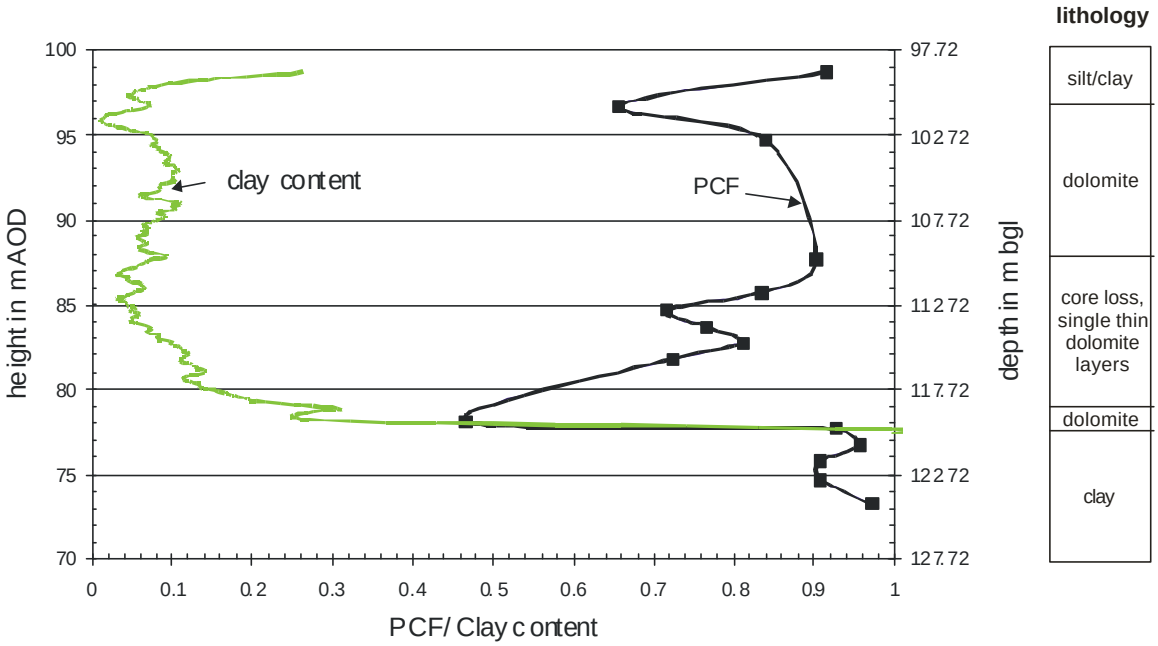


Figure 78: Depth profiles of PCF and clay content for UFZ 401

7.3.3 Discussion

The presence of SCAP in this deep aquifer system long after injection has been discontinued could clearly be proven. This implies, that SCAP do not easily degrade as often stated.

It could be shown that SCAP can be used as a further helpful tool in the investigations at the sites in Profen and Deuben. To draw a clearer picture, yet more data are needed. This includes water samples which are obtained by pumping rather than bailing and the investigation/drilling of more wells.

7.4 Looking back at the chapter

Generally, all quantifiable 22 SCAP have been detected at the investigated site in various proportions. C2-SCAP were always found in higher concentrations than C3-SCAP. Trimethylphenols are predominant within the group of C3-SCAP. Together with the quantifiable 5 Propylphenols they represent 76 to 89 % of all C3 SCAP based on the comparison of the mass 136. This means, that the analysed 22 SCAP represent at least 95% of the total SCAP concentration (compare results in the appendix).

The contamination at the investigated sites is rather different and so are the geology and hydrogeology. Nonetheless, the earlier derived similar principles for the spread of SCAP appears justified in principle. It can generally be concluded, that for sites which are contaminated by SCAP additional information can be gained by using the SCAP

distribution pattern PCF and MPR. Source derived SCAP with extensive plumes can be ideally used as partitioning/reactive tracers in monitored natural attenuation. SCAP distribution pattern contain averaged information about the flow path and the aquifer condition. This greatly supports the long term prediction of the site development. Simultaneously, SCAP show a quick response in shallow aquifers as soon as aquifer recharge occurs which in turn makes them to useful tracers describing the maximum extent of the organic plume. Site investigation should therefore be carried out well beyond the source. From the PCF it can further be concluded if degradation processes occur. Since some SCAP compounds are oxygen sensitive, their disappearance may be used as oxygen marker.

8 Outlook

> "Every scientific fulfilment raises new questions; it asks to be surpassed and outdated."
>
> **- Max Weber -**

The work was intended to investigate the environmental behaviour of SCAP in the subsurface. It may have answered some of questions but may have left as many open.

Most of all, degradation experiments and toxicity data are needed for the individual SCAP compounds to better understand and evaluate their impact on groundwater quality and its development. So remains subject to further investigations on a homogenous well investigated aquifer if the group of SCAP does not even contain more valuable information on the aquifer conditions. All here investigated sites will be monitored in future and with more data the picture about SCAP will become clearer.

The principles shown in this study on the transport behaviour of SCAP may also be applicable to other readily soluble organic contaminates. Form literature data it was even seen, that other soluble organics have steplike isotherms.

The laboratory batch experiments may be completed by column studies. The observed isotherm could further be modelled by the combined Freundlich-Langmuir-Isotherm.

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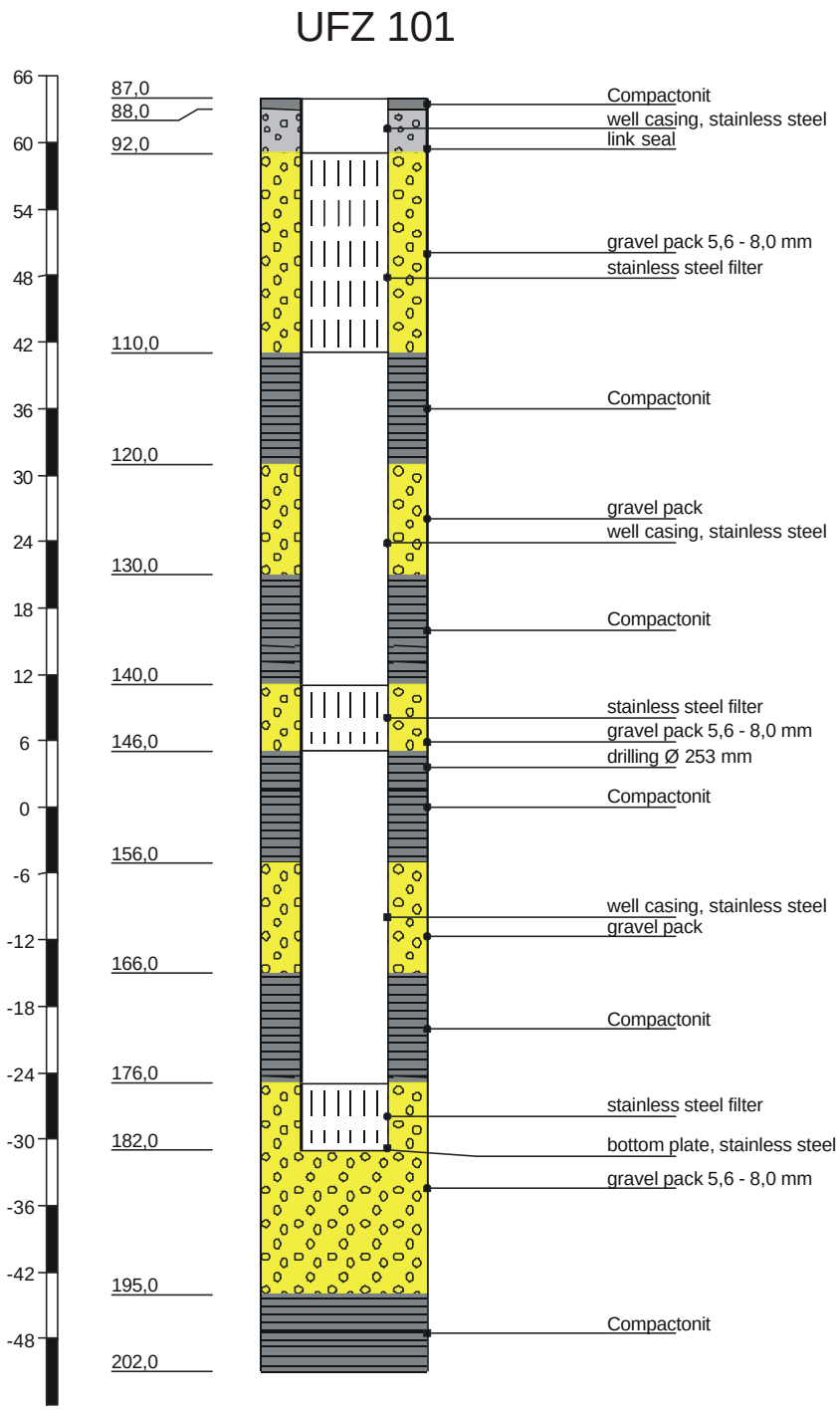
Appendix I

- **well design of the observation wells at Deuben and Profen (UFZ 101- UFZ 601)**
- **SCAP data as analysed in the drilling cores in Deuben and Profen**

well design

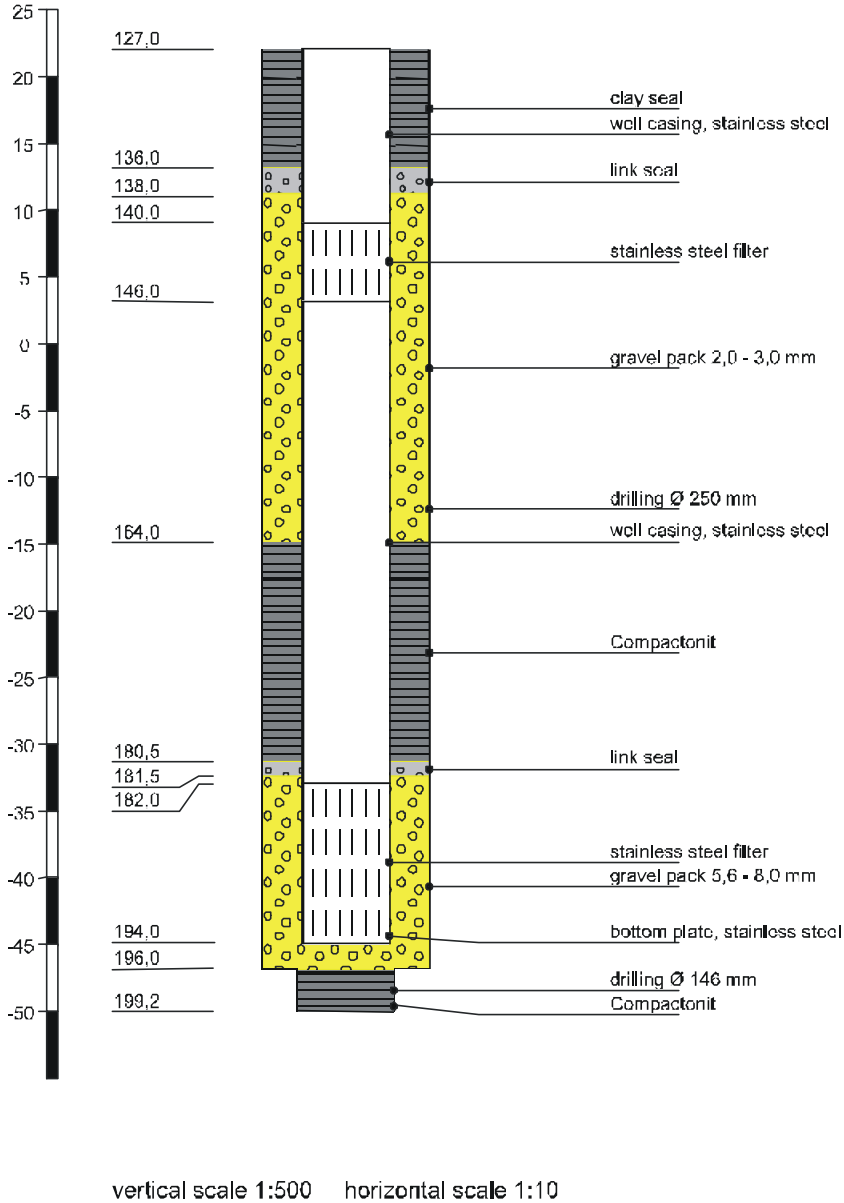
project:	research drillings Profen-Deuben	x coordinate:	4514041
drilling:	UFZ 101	y coordinate:	5665475



vertical scale 1:200 horizontal scale 1:10

well design			
project:	research drillings Profen-Deuben	x coordinate:	4514258
drilling:	UFZ 301	y coordinate:	5666161

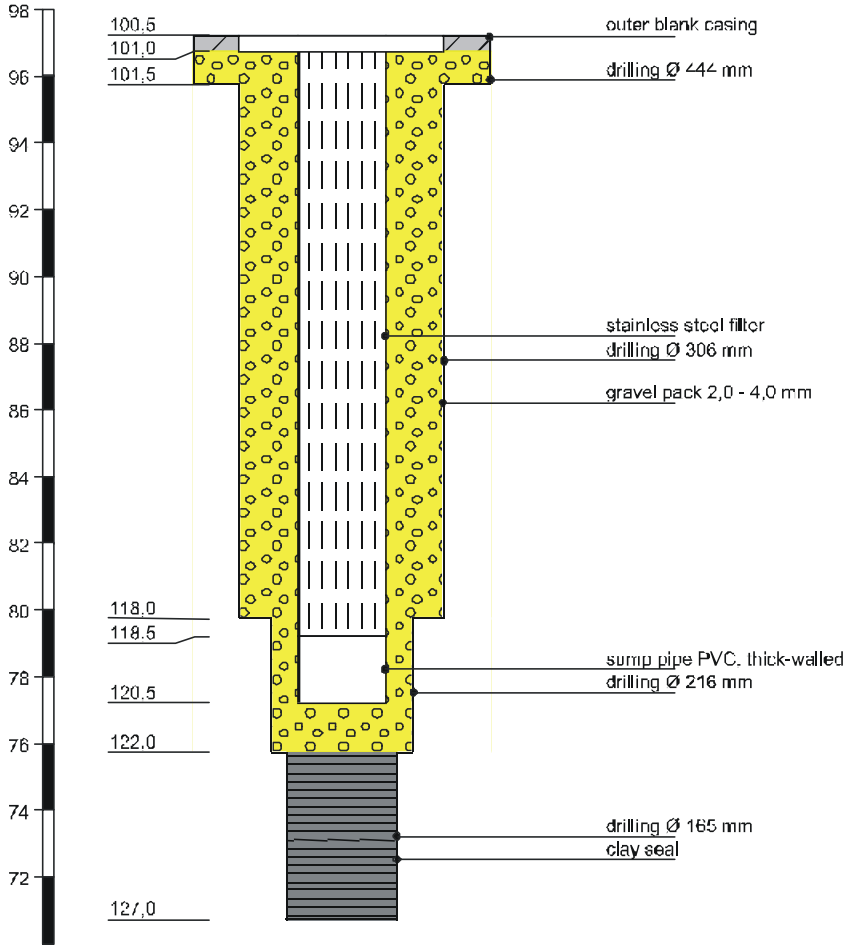
UFZ 301



vertical scale 1:500 horizontal scale 1:10

well design			
project:	research drillings Profen-Deuben	x coordinate:	4504230
drilling:	UFZ 401	y coordinate:	5662616

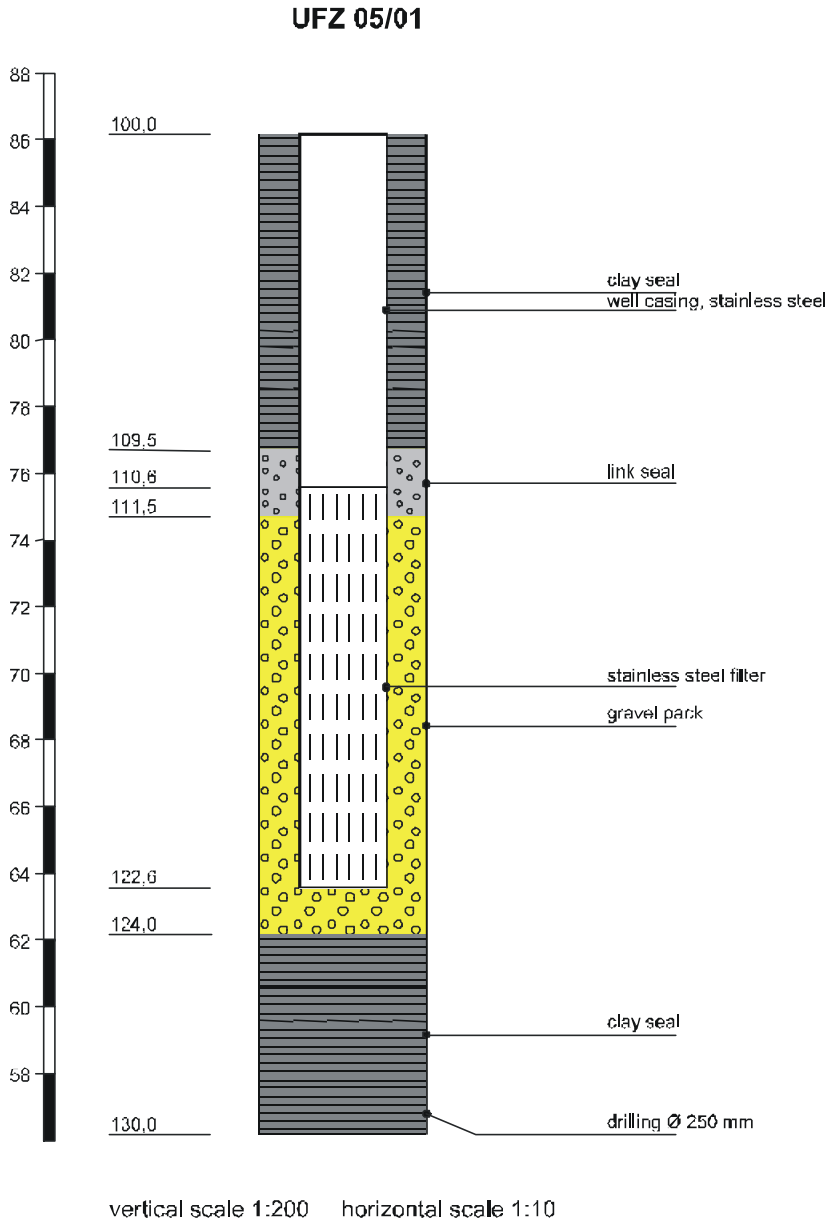
UFZ 401



vertical scale 1:200 horizontal scale 1:10

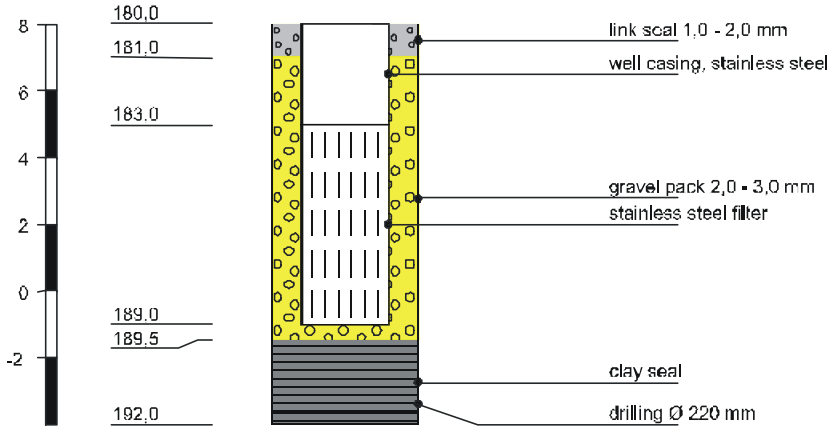
well design

project:	research drillings Profen-Deuben	x coordinate:	4505547
drilling:	UFZ 501	y coordinate:	5664266



well design			
project:	research drillings Profen-Deuben	x coordinate:	4506483
drilling:	UFZ 601	y coordinate:	5664959

UFZ 601



vertical scale 1:200 horizontal scale 1:10

UFZ 101, water content, C0 - C1 concentration data in µg/kg, PCF, corrected PCF (C) and MPR

depth in m	H_2O in %	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	PCF (c)	MPR
91	3.00	413 ± 7.8	279 ± 6.37	248 ± 0.55	531 ± 18.1	0.498	0.498	2.143
92	4.11	421 ± 10.9	326 ± 1.85	269 ± 3.12	623 ± 16.0	0.453	0.453	2.315
94	2.01	592 ± 10.9	304 ± 6.85	215 ± 3.18	473 ± 24.8	0.501	0.501	2.205
96	12.23	711 ± 30.3	463 ± 2.63	285 ± 15.6	621 ± 12.6	0.457	0.511	2.176
98	4.17	1568 ± 42.3	500 ± 1.03	391 ± 12.4	920 ± 47.1	0.587	0.629	2.351
102	2.73	322 ± 0.56	421 ± 0.34	352 ± 4.17	814 ± 37.2	0.404	0.449	2.311
104	6.54	2043 ± 80.2	650 ± 8.40	513 ± 6.89	1214 ± 29.7	0.623	0.671	2.366
106	6.17	856 ± 14.7	573 ± 15.1	274 ± 6.76	1272 ± 2.90	0.532	0.559	4.635
108	3.88	463 ± 19.7	802 ± 35.4	518 ± 24.1	1932 ± 38.5	0.443	0.474	3.732
110	7.22	667 ± 14.9	568 ± 27.9	274 ± 2.96	1222 ± 48.3	0.567	0.582	4.459
111	4.78	603 ± 25.6	580 ± 0.86	166 ± 7.29	865 ± 44.7	0.527	0.559	5.212
112	8.91	2326 ± 73.0	868 ± 27.6	191 ± 6.90	1130 ± 9.44	0.715	0.734	5.932
113	4.74	1961 ± 42.6	609 ± 12.9	556 ± 7.01	986 ± 50.7	0.810	0.808	1.772
114	9.45	< 35.4	381 ± 18.4	9.3 ± 0.15	466 ± 23.8	0.505	0.796	49.94
115	8.29	2838 ± 97.6	1018 ± 27.0	816 ± 39.6	1594 ± 71.1	0.815	0.808	1.953
117	5.75	673 ± 24.7	412 ± 18.3	66.3 ± 3.35	562 ± 0.53	0.663	0.810	8.478
118	6.96	333 ± 6.14	410 ± 0.40	34.1 ± 1.68	503 ± 20.3	0.583	0.805	14.77
119	8.98	2312 ± 106	518 ± 25.8	326 ± 4.59	768 ± 29.6	0.795	0.800	2.357
120	9.16	105 ± 2.06	422 ± 12.7	16.7 ± 0.35	489 ± 4.06	0.509	0.807	29.39
121	9.41	< 35.4	542 ± 24.0	10.7 ± 0.49	609 ± 16.8	0.469	0.803	57.06
122	6.52		315 ± 15.5	11.7 ± 0.63	371 ± 17.1	0.492	0.803	31.75
123	9.14	1298 ± 43.2	891 ± 31.8	323 ± 9.56	1102 ± 50.8	0.647	0.800	3.413
124	4.76	62.8 ± 0.60	309 ± 7.64	<2.52	350 ± 14.2	0.521	0.810	156. 9
125	8.70	231 ± 6.00	869 ± 12.7	37.7 ± 1.05	935 ± 16.4	0.555	0.797	24.79
126	8.74	90.4 ± 2.73	469 ± 16.2	26.2 ± 1.39	535 ± 3.89	0.518	0.799	20.39
127	7.54	1919 ± 70.9	452 ± 0.49	245 ± 2.24	574 ± 0.21	0.772	0.809	2.348
128	7.87	3386 ± 101	695 ± 28.9	564 ± 1.20	944 ± 25.1	0.826	0.812	1.675
129	7.99	4167 ± 87.0	763 ± 6.69	678 ± 7.98	1101 ± 50.3	0.835	0.818	1.624
133	8.25	4147 ± 136	1068 ± 19.7	923 ± 31.0	1438 ± 20.0	0.770	0.783	1.558
136	8.42	< 35.4	449 ± 7.34	391 ± 19.7	619 ± 5.72	0.593	0.610	1.585
140	8.13	118 ± 5.83	12.6 ± 0.27	<2.52	10.3 ± 0.25	0.388	0.455	1.906
142	4.30	< 35.4	130 ± 3.21	39.5 ± 1.55	138 ± 5.35	0.545	0.566	3.483
146	8.43		9.4 ± 0.40	9.5 ± 0.09	10.5 ± 0.53	0.408	0.355	1.105
149	4.88		7.8 ± 0.37	8.4 ± 0.32	9.8 ± 0.33	0.516	0.518	1.168
150	5.34		34.1 ± 0.43	17.0 ± 0.45	32.1 ± 0.36	0.487	0.487	1.885
153	4.66		<2.52			0.000	0.000	1.000
155	7.16		8.9 ± 0.03	6.6 ± 0.11	10.0 ± 0.17	0.344	0.344	1.517
156	6.21		20.3 ± 0.17	13.9 ± 0.17	21.1 ± 0.35	0.506	0.506	1.520

UFZ 101, C2 concentration data in µg/kg (d = depth in meters)

d	2-EP	4-EP	3-EP	2.6-DMP	2.4-DMP	2.5-DMP	2.3-DMP	3.4-DMP	3.5-DMP
91	94.2 ± 5.07	215 ± 0.34	338 ± 2.09	39.4 ± 1.10	155 ± 4.23	109 ± 4.31	70.3 ± 3.72	75.0 ± 3.19	222 ± 9.23
92	142 ± 5.25	230 ± 10.6	521 ± 1.85	52.7 ± 0.27	193 ± 7.22	138 ± 6.64	91.4 ± 4.02	96.6 ± 4.41	278 ± 16.0
94	98.3 ± 0.32	186 ± 3.17	408 ± 4.29	43.4 ± 0.64	161 ± 7.61	116 ± 5.42	77.1 ± 2.02	83.6 ± 2.27	232 ± 10.3
96	160 ± 2.75	267 ± 4.86	477 ± 16.6	57.3 ± 0.87	269 ± 7.29	177 ± 3.11	123 ± 1.99	134 ± 1.91	396 ± 6.57
98	141 ± 7.49	265 ± 2.94	491 ± 14.0	65.2 ± 1.28	281 ± 11.6	174 ± 2.60	120 ± 6.16	137 ± 0.04	406 ± 14.0
102	156 ± 5.63	303 ± 11.1	602 ± 2.19	71.9 ± 2.61	299 ± 0.86	199 ± 6.66	127 ± 5.15	146 ± 8.30	431 ± 22.3
104	130 ± 0.30	298 ± 11.3	462 ± 21.9	92.3 ± 1.44	400 ± 7.11	223 ± 3.75	161 ± 4.54	144 ± 7.02	427 ± 12.5
106	202 ± 7.66	350 ± 2.36	827 ± 40.5	65.2 ± 2.46	237 ± 12.2	174 ± 8.86	115 ± 4.83	129 ± 1.37	375 ± 21.1
108	231 ± 4.95	739 ± 7.23	1476 ± 48.8	118 ± 3.87	402 ± 4.90	294 ± 14.2	192 ± 7.70	150 ± 3.44	639 ± 4.32
110	152 ± 5.27	293 ± 7.12	665 ± 20.9	53.3 ± 1.57	196 ± 8.11	134 ± 4.44	85.4 ± 2.24	93.0 ± 3.83	286 ± 15.9
111	128 ± 3.12	246 ± 7.24	654 ± 23.7	49.6 ± 1.84	198 ± 1.47	128 ± 2.93	82.8 ± 3.43	93.3 ± 4.02	277 ± 8.51
112	130 ± 5.65	268 ± 12.2	636 ± 10.4	55.4 ± 1.82	177 ± 3.70	130 ± 2.71	82.2 ± 2.34	88.2 ± 3.59	283 ± 10.1
113	63.4 ± 0.91	213 ± 1.46	319 ± 7.42	24.1 ± 0.78	105 ± 2.01	73.8 ± 2.63	39.1 ± 1.22	44.5 ± 2.01	132 ± 4.58
114	70.2 ± 3.64	49.9 ± 1.63	311 ± 0.64	20.7 ± 0.75	81.7 ± 1.29	57.3 ± 3.10	34.8 ± 0.85	38.3 ± 1.70	126 ± 5.21
115	93.0 ± 0.77	278 ± 10.2	502 ± 9.04	33.7 ± 0.15	156 ± 5.07	107 ± 3.65	60.1 ± 0.91	76.1 ± 0.07	201 ± 7.25
117	61.1 ± 2.68	111 ± 4.18	284 ± 4.92	22.6 ± 0.99	89.9 ± 3.34	64.9 ± 2.94	40.9 ± 1.60	49.9 ± 0.59	148 ± 2.31
118	61.8 ± 3.06	104 ± 3.48	298 ± 3.67	25.2 ± 0.81	94.0 ± 2.33	64.5 ± 3.24	42.0 ± 1.92	50.2 ± 1.32	149 ± 7.07
119	70.7 ± 3.04	170 ± 4.45	329 ± 5.54	27.4 ± 0.66	107 ± 2.63	75.3 ± 3.18	47.2 ± 0.53	54.8 ± 2.23	162 ± 3.88
120	75.1 ± 2.54	62.3 ± 0.29	324 ± 14.3	27.9 ± 0.97	113 ± 4.54	68.5 ± 2.40	45.0 ± 1.55	52.8 ± 0.93	156 ± 6.25
121	81.4 ± 4.20	59.3 ± 1.77	395 ± 18.6	33.0 ± 0.76	127 ± 2.21	83.1 ± 3.40	52.2 ± 0.88	61.4 ± 2.42	184 ± 4.84
122	48.7 ± 2.43	38.4 ± 0.50	235 ± 4.41	19.4 ± 0.39	81.1 ± 1.63	49.6 ± 0.43	31.4 ± 1.48	38.7 ± 2.20	115 ± 4.17
123	143 ± 0.13	222 ± 3.33	617 ± 15.1	63.4 ± 2.15	234 ± 3.61	151 ± 2.54	90.7 ± 4.81	102 ± 1.99	303 ± 6.41
124	47.6 ± 0.33	42.2 ± 1.50	203 ± 10.7	19.4 ± 0.08	78.6 ± 3.60	48.4 ± 2.39	31.4 ± 1.41	38.0 ± 1.74	113 ± 2.65
125	109 ± 2.18	106 ± 0.26	557 ± 23.5	56.2 ± 1.78	202 ± 7.80	127 ± 5.15	78.4 ± 2.61	85.9 ± 0.79	264 ± 4.97
126	72.0 ± 3.19	69.1 ± 1.61	367 ± 15.4	26.8 ± 0.58	111 ± 3.36	73.0 ± 3.93	48.5 ± 2.56	56.7 ± 0.21	165 ± 4.30
127	67.0 ± 1.26	150 ± 1.94	322 ± 1.94	26.3 ± 0.79	104 ± 2.76	74.3 ± 0.35	47.5 ± 2.64	51.4 ± 0.50	151 ± 5.76
128	84.6 ± 1.40	234 ± 12.2	372 ± 7.74	36.7 ± 0.76	142 ± 5.50	91.6 ± 3.13	61.4 ± 0.25	56.3 ± 2.92	167 ± 2.87
129	92.5 ± 1.27	276 ± 7.61	442 ± 1.40	35.4 ± 0.55	152 ± 3.31	101 ± 4.01	70.9 ± 2.01	63.8 ± 3.62	189 ± 5.42
133	154 ± 4.96	437 ± 22.2	794 ± 12.3	66.4 ± 0.74	247 ± 6.89	162 ± 8.15	107 ± 3.46	105 ± 3.79	311 ± 3.82
136	54.6 ± 0.68	184 ± 2.44	345 ± 18.2	25.4 ± 0.15	86.6 ± 0.58	65.0 ± 0.76	42.6 ± 0.65	43.1 ± 0.15	120 ± 6.91
140	6.73 ± 0.26	7.70 ± 0.33	11.2 ± 0.15	24.3 ± 0.21	57.1 ± 1.70	23.1 ± 0.10	19.7 ± 0.68	9.52 ± 0.47	28.2 ± 1.09
142	18.9 ± 0.04	17.3 ± 0.51	47.2 ± 0.95	14.2 ± 0.56	41.2 ± 1.11	24.1 ± 0.15	16.9 ± 0.50	16.8 ± 0.13	49.8 ± 2.69
146	3.81 ± 0.06	9.07 ± 0.31	9.15 ± 0.17	7.07 ± 0.27	6.23 ± 0.16	3.73 ± 0.11	2.50 ± 0.11	1.76 ± 0.02	5.12 ± 0.01
149	1.44 ± 0.01	3.82 ± 0.20	0.00 ± 0.00	3.93 ± 0.06	3.60 ± 0.10	1.91 ± 0.05	<1.68	<1.68	3.30 ± 0.16
150	5.24 ± 0.22	27.4 ± 0.38	17.6 ± 0.79	5.79 ± 0.26	12.0 ± 0.51	7.82 ± 0.34	3.43 ± 0.10	2.10 ± 0.02	6.23 ± 0.01
153	<4.20			<1.68					
155	2.93 ± 0.11	5.07 ± 0.25	6.53 ± 0.31	5.48 ± 0.04	5.41 ± 0.06	2.73 ± 0.11	2.17 ± 0.06	1.77 ± 0.09	5.24 ± 0.00
156	3.18 ± 0.11	13.7 ± 0.31	9.05 ± 0.20	5.62 ± 0.10	8.51 ± 0.08	4.61 ± 0.07	2.57 ± 0.00	1.60 ± 0.09	4.74 ± 0.21

UFZ 101, C3 concentration data in µg/kg and total SCAP (d = depth in meters)

d	2.4.6 TMP	2.3.6 TMP	2.3.5 TMP	3.4.5 TMP	2i-PP	2n-PP	4i-PP	3i-PP	4n-PP	total amount
91	21.7 ± 0.41	25.0 ± 0.11	126 ± 3.97	18.1 ± 0.68	6.43	31.64	129.89	2.70	54.14	2792 ± 71.3
92	30.8 ± 0.71	35.1 ± 0.16	181 ± 6.07	24.7 ± 0.95	5.88	26.47	172.93	3.76	64.42	3505 ± 96.2
94	25.6 ± 1.27	30.5 ± 1.46	142 ± 6.69	19.6 ± 0.72	5.53	24.67	150.52	2.80	57.09	2855 ± 91.8
96	34.7 ± 0.91	37.9 ± 0.67	234 ± 0.14	33.8 ± 0.97	13.19	62.67	270.86	4.86	31.00	4151 ± 110
98	36.9 ± 0.70	45.1 ± 0.33	245 ± 11.8	34.9 ± 2.33	11.73	40.45	240.15	5.37	99.69	4649 ± 178
102	40.4 ± 0.27	53.1 ± 3.51	294 ± 1.57	37.0 ± 0.33	12.17	62.34	268.14	5.34	106.66	4802 ± 113
104	49.4 ± 0.92	63.6 ± 1.90	159 ± 10.3	43.9 ± 2.94	16.63	82.34	338.70	7.88	134.92	5611 ± 211
106	27.6 ± 1.57	32.1 ± 0.69	242 ± 10.2	24.1 ± 1.58	5.79	23.65	169.62	2.97	63.03	5185 ± 155
108	56.6 ± 2.82	70.6 ± 1.33	378 ± 21.7	50.6 ± 1.37	12.17	60.93	364.87	5.92	143.57	8636 ± 244
110	32.4 ± 1.48	22.0 ± 0.38	154 ± 9.13	166 ± 8.24	4.55	21.49	121.99	1.18	47.49	4593 ± 183
111	15.7 ± 0.08	24.2 ± 0.18	187 ± 6.62	17.9 ± 0.90	5.22	25.34	136.14	<0.96	54.97	3934 ± 142
112	14.5 ± 0.13	18.1 ± 0.54	145 ± 8.86	11.2 ± 0.44	4.05	18.14	95.97		40.69	4386 ± 179
113	6.19 ± 0.31	7.35 ± 0.29	64.2 ± 3.71	5.28 ± 0.31	2.00	8.34	44.89		20.14	3324 ± 141
114	5.70 ± 0.23	6.43 ± 0.23	63.0 ± 0.38	5.07 ± 0.16	1.72	9.39	43.55		18.51	1799 ± 62.2
115	7.86 ± 0.42	9.11 ± 0.57	87.5 ± 0.81	7.42 ± 0.15	2.39	11.21	61.80		25.53	5149 ± 274
117	6.46 ± 0.14	7.39 ± 0.45	70.8 ± 3.69	4.99 ± 0.15	2.47	11.14	46.33		21.11	2083 ± 74.8
118	7.29 ± 0.24	9.37 ± 0.08	81.7 ± 5.10	6.25 ± 0.12	2.66	10.72	53.22		23.13	2030 ± 60.9
119	6.44 ± 0.29	9.38 ± 0.19	86.0 ± 0.81	6.88 ± 0.13	2.81	13.55	56.94		25.63	2863 ± 193
120	9.49 ± 0.24	11.5 ± 0.72	90.9 ± 4.03	6.52 ± 0.17	3.02	12.14	62.30		25.69	2075 ± 58.1
121	10.0 ± 0.59	12.2 ± 0.15	102 ± 2.34	7.61 ± 0.31	9.40	37.87	187.09		79.37	2684 ± 83.7
122	6.61 ± 0.43	7.88 ± 0.23	64.1 ± 0.04	6.22 ± 0.06	2.25	9.21	46.02		19.41	1517 ± 51.6
123	18.8 ± 0.30	24.0 ± 1.20	163 ± 1.08	14.4 ± 0.07	6.46	14.48	126.48		56.67	4668 ± 178
124	6.17 ± 0.21	6.97 ± 0.13	60.1 ± 0.44	4.04 ± 0.03	2.07	7.75	37.61		16.28	1423 ± 47.7
125	15.3 ± 0.20	19.1 ± 0.30	135 ± 1.71	10.5 ± 0.28	4.04	19.20	97.17		39.37	3767 ± 87.8
126	6.11 ± 0.10	8.30 ± 0.04	78.9 ± 3.68	7.01 ± 0.19	2.69	12.53	58.08		24.66	2216 ± 63.4
127	6.83 ± 0.18	8.07 ± 0.33	74.5 ± 0.86	5.98 ± 0.00	2.49	10.17	50.89		22.05	2444 ± 93.1
128	11.8 ± 0.02	12.3 ± 0.68	87.9 ± 1.07	7.26 ± 0.16	3.30	12.08	63.58		26.98	3673 ± 195
129	9.39 ± 0.59	10.9 ± 0.65	89.8 ± 5.63	7.79 ± 0.51	3.20	12.00	63.15		27.43	4190 ± 189
133	13.6 ± 0.50	20.6 ± 1.23	161 ± 7.00	16.0 ± 0.92	5.31	23.87	120.79		52.75	6226 ± 283
136	6.75 ± 0.35	7.26 ± 0.11	67.4 ± 3.35	14.7 ± 0.03	2.07	11.93	51.71		20.35	2608 ± 67.1
140	6.67 ± 0.30	8.37 ± 0.32	11.2 ± 0.60	3.91 ± 0.18	2.07	10.36	45.52		9.42	308 ± 12.7
142	2.82 ± 0.02	4.12 ± 0.12	12.1 ± 0.19	2.38 ± 0.02	<0.96	1.51	21.84		4.63	603 ± 17.1
146	2.97 ± 0.11	4.68 ± 0.01	4.83 ± 0.21	1.06 ± 0.07	<0.96					92 ± 2.64
149	1.34 ± 0.04	2.40 ± 0.02	2.97 ± 0.14	<0.96						54 ± 1.87
150	1.25 ± 0.05	2.72 ± 0.08	4.04 ± 0.24	<0.96	<0.96	2.47	5.06	<0.96	<0.96	187 ± 4.27
153	<0.96									
155	1.55 ± 0.07	3.14 ± 0.00	4.58 ± 0.10	0.96 ± 0.06	<0.96	<0.96	7.83	<0.96	<0.96	85 ± 1.58
156	1.57 ± 0.06	2.50 ± 0.08	6.49 ± 0.42	<0.96	<0.96	3.84	5.07	<0.96	2.34	131 ± 2.44

UFZ 301, water content, C0 - C1 concentration data in µg/kg, PCF and MPR

depth in m	H_2O in %	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	MPR
137	6.89	< 35.4	<2.52			0.000	
138	4.82		134.0 ± 3.01	113 ± 5.33	14.1 ± 0.44	0.628	0.124
139	7.51		42.3 ± 0.01	31.1 ± 0.51	2.18 ± 0.06	0.657	0.070
144	5.93	2302 ± 51.4	418.5 ± 0.11	165 ± 5.00	320 ± 9.42	0.832	1.940
146	2.63	550 ± 3.82	100.8 ± 5.37	59.7 ± 1.06	130 ± 2.28	0.827	2.184
148	1.60	523 ± 10.7	174.2 ± 7.93	116 ± 7.63	199 ± 3.32	0.740	1.720
150	2.04	2038 ± 18.7	497.2 ± 34.1	172 ± 5.29	487 ± 20.5	0.766	2.826
152	3.40	1715 ± 47.3	415.0 ± 8.77	104 ± 5.10	371 ± 25.5	0.759	3.573
153	6.32	782 ± 1.19	237.1 ± 15.1	227 ± 1.20	335 ± 13.0	0.964	1.475
154	2.33	< 35.4	<2.52				
157	10.94						
158	11.54						
160	9.13						
179	4.04	20751 ± 1047	2599.1 ± 28.8	2391 ± 116	3213 ± 94.4	0.980	1.344
180	4.46	2389 ± 40.5	30.0 ± 1.00	26.8 ± 0.42	28.0 ± 0.87	0.997	1.045
181	3.94	912 ± 4.6	<2.52			1.000	
182	12.84	21128 ± 150	2437.4 ± 109	2220 ± 96.2	3226 ± 192	0.951	1.453
183	5.45	2954 ± 6.14	585.1 ± 25.7	526 ± 34.5	629 ± 29.0	0.942	1.196
184	8.04	16138 ± 187	2293.7 ± 85.1	2036 ± 101	2895 ± 202	0.893	1.422
185	3.89	8110 ± 127	1409.4 ± 2.99	1348 ± 72.7	1977 ± 35.4	0.879	1.467
186	3.34	< 35.4	<2.52				
187	3.65						
189	5.50	10125 ± 245	1244.5 ± 56.5	1163 ± 17.4	1645 ± 38.4	0.941	1.415
190	7.76	18088 ± 914	2615.5 ± 77.6	2359 ± 34.2	3428 ± 213	0.919	1.453
191	3.87	9409 ± 118	1183.1 ± 22.7	1057 ± 69.3	1747 ± 110	0.930	1.654
192	2.19	< 35.4	<2.52				

UFZ 301, C2 concentration data in µg/kg (d = depth in meters)

d	2-EP	4-EP	3-EP	2,6-DMP	2,4-DMP	2,5-DMP	2,3-DMP	3,4-DMP	3,5-DMP
137	5.28 ± 0.43	<4.20	<4.20	<1.68					
138	10.1 ± 0.66	29.3 ± 2.37	28.5 ± 2.03	3.07 ± 0.16	14.2 ± 0.66	12.2 ± 0.72	8.74 ± 0.41	8.78 ± 0.42	31.7 ± 0.45
139	<4.20	6.67 ± 0.27	4.05 ± 0.20	<1.68	2.88 ± 0.06	3.09 ± 0.00	2.53 ± 0.16	2.83 ± 0.08	12.8 ± 0.54
144	42.3 ± 1.75	49.8 ± 3.78	162 ± 1.42	17.1 ± 0.19	75.5 ± 3.78	46.7 ± 1.58	27.7 ± 0.50	35.0 ± 2.30	111 ± 8.29
146	14.2 ± 0.32	29.0 ± 0.39	63.2 ± 2.14	1.86 ± 0.07	9.27 ± 0.48	10.4 ± 0.25	6.22 ± 0.30	5.19 ± 0.32	27.5 ± 0.57
148	24.1 ± 0.71	54.4 ± 2.27	114 ± 4.49	6.85 ± 0.37	28.8 ± 0.77	21.5 ± 0.72	14.0 ± 0.51	14.5 ± 0.58	48.1 ± 1.95
150	58.1 ± 3.31	76.2 ± 2.21	278 ± 12.2	28.6 ± 1.96	103 ± 5.79	65.9 ± 1.19	39.5 ± 2.23	48.2 ± 2.06	145 ± 4.26
152	54.8 ± 3.04	39.6 ± 1.09	244 ± 6.73	23.7 ± 0.92	84.4 ± 4.47	57.6 ± 0.38	34.3 ± 1.73	37.5 ± 0.64	131 ± 8.20
153	<4.20	9.21 ± 0.34	10.9 ± 0.18	<1.68	7.79 ± 0.04	3.62 ± 0.05	4.21 ± 0.27	6.00 ± 0.22	12.6 ± 0.51
154	<4.20			<1.68					
157									
158									
160									
179	26.5 ± 0.77	86.7 ± 6.03	130 ± 3.41	11.3 ± 0.21	64.2 ± 1.04	35.5 ± 2.42	54.1 ± 0.47	92.7 ± 2.72	89.0 ± 4.68
180	<4.20			<1.68	2.27 ± 0.12	<1.68	<1.68	<1.68	3.60 ± 0.24
181				<1.68					
182	77.0 ± 6.18	257 ± 18.4	465 ± 34.1	29.1 ± 1.37	129 ± 6.79	87.1 ± 6.08	85.1 ± 1.96	116 ± 5.02	214 ± 8.53
183	13.5 ± 0.68	34.6 ± 2.77	67.4 ± 3.13	4.34 ± 0.22	24.3 ± 0.13	13.4 ± 0.17	16.8 ± 0.19	22.1 ± 0.92	85.3 ± 5.40
184	171 ± 12.6	607 ± 6.39	605 ± 44.1	88.5 ± 6.45	304 ± 4.78	200 ± 11.8	137 ± 7.66	167 ± 2.70	300 ± 15.7
185	95.6 ± 2.20	366 ± 27.2	481 ± 40.9	46.0 ± 0.75	160 ± 11.0	113 ± 0.26	88.8 ± 0.96	112 ± 7.43	189 ± 3.87
186	<4.20			<1.68					
187									
189	44.3 ± 2.66	169 ± 3.93	225 ± 2.61	21.3 ± 1.31	88.4 ± 5.33	55.3 ± 1.85	54.4 ± 2.54	68.2 ± 0.13	123 ± 1.72
190	144 ± 5.34	475 ± 31.8	619 ± 52.8	59.2 ± 1.51	215 ± 1.38	151 ± 9.40	126 ± 5.04	160 ± 11.0	271 ± 0.58
191	49.8 ± 1.50	159 ± 9.46	297 ± 17.9	22.6 ± 0.74	82.9 ± 0.27	55.9 ± 0.01	51.8 ± 2.51	109 ± 2.15	122 ± 7.66
192	<4.20			<1.68					

UFZ 301, C3 concentration data in µg/kg and total SCAP (d = depth in meters)

d	2.4.6 TMP	2.3.6 TMP	2.3.5 TMP	3.4.5 TMP	2i-PP	2n-PP	4i-PP	3i-PP	4n-PP	total SCAP
137	<0.96		1.78 ± 0.01	<0.96						10.5 ± 0.50
138			6.92 ± 0.48							416.0 ± 16.8
139			1.09 ± 0.03							115.0 ± 2.0
144	2.85 ± 0.06	3.26 ± 0.15	46.5 ± 2.38	3.24 ± 0.23	<0.96	1.99	15.61	<0.96	6.19	3851.8 ± 91.9
146	<0.96	<0.96	7.35 ± 0.18	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	1016.1 ± 17.3
148	0.92 ± 0.04	1.25 ± 0.09	22.8 ± 1.29	1.50 ± 0.05	<0.96	<0.96	2.75	<0.96	1.03	1369.0 ± 42.9
150	5.13 ± 0.03	6.95 ± 0.23	78.0 ± 3.44	5.56 ± 0.09	1.34	4.68	17.80	<0.96	12.56	4168.9 ± 115
152	4.73 ± 0.22	6.12 ± 0.31	74.4 ± 5.60	4.92 ± 0.36	<0.96	2.86	17.89	<0.96	7.61	3429.7 ± 119
153	<0.96									1640.7 ± 32.2
154										0 ± 0
157										0 ± 0
158										0 ± 0
160										0 ± 0
179	<0.96	<0.96	2.12 ± 0.08	1.31 ± 0.06	<0.96	<0.96	<0.96	<0.96	<0.96	29547.4 ± 1308
180	<0.96									2481.6 ± 43.3
181										912.0 ± 4.64
182	<0.96	<0.96	34.5 ± 0.48	4.15 ± 0.11	<0.96	<0.96	<0.96	<0.96	<0.96	30510.2 ± 634
183	<0.96	<0.96	4.11 ± 0.30	<0.96	<0.96	<0.96	<0.96	<0.96	<0.96	4980 ± 109
184	8.33 ± 0.26	12.2 ± 0.46	168 ± 2.60	12.0 ± 0.85	<0.96	2.37	19.65	<0.96	7.80	26171.6 ± 684
185	1.51 ± 0.02	2.69 ± 0.20	104 ± 3.42	7.00 ± 0.17	<0.96	<0.96	5.00	<0.96	<0.96	14616.1 ± 336
186	<0.96									0 ± 0
187										0 ± 0
189	<0.96	<0.96	37.6 ± 1.76	3.46 ± 0.06	<0.96					15068.3 ± 379
190	1.61 ± 0.04	2.62 ± 0.18	102 ± 5.00	7.87 ± 0.19						28825.0 ± 1358
191	<0.96	1.33 ± 0.03	51.5 ± 2.47	3.33 ± 0.20						14403.3 ± 362
192	<0.96									0 ± 0

UFZ 401, water content, C0 - C1 concentration data in µg/kg, PCF and MPR

depth in m	H_2O in %	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	MPR
80	10.5	137 ± 3.31	37.7 ± 1.6	18.4 ± 0.9	53.9 ± 0.3	0.632	2.929
83	9.8	< 35.4	<2.52				
87	10.9						
90	11.2	1411 ± 57.4	127 ± 4.7	144 ± 0.2	228 ± 4.8	0.718	1.583
94	8.4	31320 ± 598	3110 ± 38	5180 ± 23	5370 ± 22	0.778	1.037
97	9.2	4521 ± 141	326 ± 0.3	531 ± 24	548 ± 3.8	0.828	1.032
99	12.1	77076 ± 1260	8410 ± 263	14800 ± 361	15100 ± 502	0.298	1.020
101	14.5	8295 ± 186	1300 ± 61	2240 ± 2.9	2510 ± 51	0.255	1.121
103	4.74	6946 ± 315	792 ± 18	1440 ± 39	1490 ± 6.2	0.282	1.035
110	2.12	8950 ± 310	988 ± 5.3	1700 ± 36	1800 ± 77	0.295	1.059
112	15.2	6822 ± 112	1020 ± 49	1820 ± 50	1900 ± 7	0.329	1.044
113	0.36	957.3 ± 21.3	144 ± 2.2	200 ± 1.8	214 ± 0.2	0.246	1.070
114	11.2	1509 ± 65.3	267 ± 0.8	400 ± 9.6	446 ± 4.5	0.307	1.115
115	3.58	2311 ± 68.8	339 ± 3.6	579 ± 21	571 ± 10	0.304	0.986
115.9	8.25	874 ± 12.1	147 ± 0.7	213 ± 2.6	239 ± 11	0.276	1.122
119.6	3.72	1506 ± 37.7	507 ± 10	1420 ± 55	2210 ± 33	0.312	1.556
120	8.43	22986 ± 294	2680 ± 116	4460 ± 175	4610 ± 221	0.308	1.034
121	10.1	12100 ± 487	961 ± 2.3	1420 ± 53	1520 ± 29	0.231	1.070
122	10.8	51640 ± 804	6290 ± 281	10300 ± 188	10600 ± 381	0.307	1.029
123	10.2	32850 ± 1400	3820 ± 68	6460 ± 54	7150 ± 160	0.308	1.107
124.5	13.5	16000 ± 278	1370 ± 36	1920 ± 72	2060 ± 58	0.242	1.073
125	6.76	< 35.4	<2.52				
126	9.04						
127	13.7						

UFZ 401, C2 concentration data in µg/kg (d = depth in meters)

d	2-EP	4-EP	3-EP	2,6-DMP	2,4-DMP	2,5-DMP	2,3-DMP	3,4-DMP	3,5-DMP
80	6.6 ± 0.2	14.2 ± 0.1	12.3 ± 0.3	1.7 ± 0.1	6.71 ± 0.1	5.99 ± 0.3	4.7 ± 0.1	<1.68	9.61 ± 0.3
83	<4.20			<1.68					
87									
90	16 ± 0.2	56.6 ± 0.9	28.4 ± 0.5	4 ± 0.1	22.2 ± 0.6	17.3 ± 0.2	14 ± 0.3		29.8 ± 1.1
94	263 ± 9.4	1140 ± 47	509 ± 21	84 ± 2.2	579 ± 7.1	348 ± 7.8	282 ± 12		595 ± 7.2
97	21 ± 0.1	95.2 ± 2.9	38.5 ± 0.9	6 ± 0.3	38.7 ± 1.1	25.1 ± 0.9	21 ± 0.1	<1.68	41 ± 0.8
99	888 ± 24	3540 ± 0	1800 ± 38	302 ± 3.4	2000 ± 65	1190 ± 39	941 ± 12		2010 ± 65
101	464 ± 11	2450 ± 88	1080 ± 1.6	140 ± 3.2	1141 ± 24	614 ± 31	502 ± 14		1540 ± 58
103	149 ± 6.6	724 ± 6.8	233 ± 11	41 ± 1.1	318 ± 23	191 ± 1.2	160 ± 2.8	210 ± 8.2	306 ± 9.8
110	132 ± 5.5	510 ± 25	270 ± 6.5	29 ± 0.6	203 ± 3.7	153 ± 1.8	129 ± 4.7	114 ± 1.7	204 ± 8.2
112	195 ± 5.9	758 ± 24	419 ± 20	47 ± 0.9	318 ± 12	239 ± 3.4	202 ± 5.9	177 ± 5.5	348 ± 4.1
113	69 ± 0.9	149 ± 5.5	86.1 ± 1.1	29 ± 1.3	98.5 ± 4.5	60.7 ± 2.1	45 ± 2.3	31.5 ± 1.6	102 ± 4.4
114	91 ± 2.1	213 ± 2.7	63.1 ± 1.5	27 ± 0.6	127 ± 1.5	81.9 ± 3.4	73 ± 2.1	72.8 ± 2	156 ± 1.5
115	84 ± 1.9	252 ± 4.9	110 ± 3.4	29 ± 0.9	150 ± 4.8	88.9 ± 2.2	79 ± 3.3	69.3 ± 2.6	140 ± 6.4
115.9	64 ± 0.3	115 ± 5.2	53.3 ± 1.3	20 ± 0.1	88.8 ± 3.7	55.3 ± 1.7	57 ± 0.1	59.1 ± 2	105 ± 1.8
119.6	608 ± 30	1620 ± 68	1160 ± 25	271 ± 14	958 ± 36	680 ± 22	503 ± 17	245 ± 2.5	972 ± 1.4
120	274 ± 5.6	911 ± 44	344 ± 3.3	91 ± 0.8	467 ± 17	328 ± 8.9	259 ± 12	249 ± 2.2	393 ± 7.2
121	66 ± 0.2	205 ± 7.1	119 ± 4.8	22 ± 1.0	120 ± 3.6	77.6 ± 1.0	87 ± 0.9	75 ± 0.1	107 ± 5.1
122	731 ± 35	2500 ± 38	1310 ± 40	175 ± 2.3	1400 ± 43	814 ± 4.4	653 ± 4.5	1050 ± 35	961 ± 43
123	484 ± 21	1760 ± 87	864 ± 40	125 ± 3.8	876 ± 27	548 ± 18	387 ± 29	348 ± 15	704 ± 5.7
124.5	61 ± 0.6	150 ± 7.2	106 ± 2.2	20 ± 0.3	112 ± 0.5	74.1 ± 0.1	86 ± 1.4	62.4 ± 0.7	95.1 ± 0.7
125	<4.20			<1.68					
126									
127									

UFZ 401, C3 concentration data in µg/kg and total SCAP (d = depth in meters), no propylphenols present

d	2,4,6 TMP	2,3,6 TMP	2,3,5 TMP	3,4,5 TMP	total amount
80	<0.96	<0.96	1.2 ± 0	<0.96	174 ± 7.5
83	<0.96				
87					
90	1.1 ± 0	1.51 ± 0	3.6 ± 0.1	2 ± 0	695 ± 71.1
94	15 ± 0.2	18.4 ± 0.8	46 ± 1.6	29 ± 0.2	17568 ± 797
97	<0.96	1.11 ± 0	2.5 ± 0.1	1.7 ± 0.1	1697 ± 175.8
99	84 ± 0.9	81.2 ± 0.7	187 ± 5.7	120 ± 2.7	128529 ± 2642
101	299 ± 8.1	252 ± 9.5	564 ± 22	315 ± 0.3	23706 ± 571
103	33 ± 1.2	40.9 ± 0.4	91 ± 4.3	54 ± 2.2	13219 ± 457
110	6.4 ± 0.2	8.8 ± 0.1	28 ± 1	13 ± 0.3	15238 ± 487
112	16 ± 0.3	24.5 ± 1.2	72 ± 0.1	38 ± 1	14415 ± 302
113	16 ± 0.6	23.8 ± 0.9	31 ± 0.1	11 ± 0.3	2267 ± 51.1
114	19 ± 0.1	18 ± 0.3	43 ± 0.7	15 ± 0.5	3622 ± 99.2
115	16 ± 0.1	23 ± 0.3	38 ± 1.6	17 ± 0.4	4895 ± 136
115.9	15 ± 0.3	15.5 ± 0.3	35 ± 1.5	12 ± 0.4	2168 ± 44.8
119.6	106 ± 4.8	178 ± 4.6	234 ± 5.2	93 ± 3.9	13271 ± 369
120	13 ± 0.2	14.1 ± 0.4	38 ± 0.6	28 ± 0.4	38145 ± 909
121	2 ± 0.1	3.5 ± 0.1	6.4 ± 0	5.6 ± 0.1	16898 ± 596
122	34 ± 1.4	27.6 ± 0.9	97 ± 3.1	73 ± 1.3	88656 ± 1905
123	25 ± 0.7	27.6 ± 0.9	81 ± 2.1	52 ± 2.5	56561 ± 1935
124.5	<0.96		2.8 ± 0.1	<0.96	22120 ± 458
125	<0.96				
126					
127					

UFZ 501, water content, C0 - C1 concentration data in µg/kg, PCF and MPR

depth in m	H_2O in %	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	MPR
103	1.30	< 35.4	<2.52				
105	1.20	49.3 ± 1.02	10.2 ± 0.18	8.58 ± 0.16	3.76 ± 0.03	0.603	0.438
106	1.80	< 35.4	<2.52	1.69 ± 0.05	5.86 ± 0.04		3.466
107	1.10		2.59 ± 0.02	2.10 ± 0.03	2.81 ± 0.10		1.333
108	1.20		<2.52	1.89 ± 0.03	3.00 ± 0.08		1.587
110	1.90	312 ± 1.71	7.99 ± 0.07	11.6 ± 0.35	14.1 ± 0.59	2.097	1.213
113	1.90	183 ± 6.41	8.40 ± 0.18	7.82 ± 0.02	10.2 ± 0.04	2.031	1.301
115	2.20	401 ± 5.62	3.64 ± 0.03	4.60 ± 0.15	4.96 ± 0.11	7.050	1.078
116	2.10	220 ± 5.89	4.74 ± 0.02	6.10 ± 0.27	7.77 ± 0.15	2.306	1.273
117	2.20	473 ± 14.5	16.1 ± 0.21	15.4 ± 0.03	19.9 ± 0.86	1.053	1.289
118	1.70	184 ± 2.32	5.01 ± 0.14	6.52 ± 0.16	7.72 ± 0.20	2.174	1.184
119	1.50	140 ± 2.10	24.0 ± 0.82	18.2 ± 0.88	26.8 ± 1.28	0.160	1.472
123	1.40	76.8 ± 3.18	11.6 ± 0.16	10.4 ± 0.13	13.7 ± 0.45	0.581	1.323
124	1.90	90.2 ± 0.98	21.7 ± 0.01	15.9 ± 0.79	16.7 ± 0.41	0.787	1.052
125	1.40	65.4 ± 1.92	134 ± 4.55	127 ± 4.39	170 ± 6.90	0.271	1.331
126	6.20	55091 ± 92.1	3839 ± 53.2	4313 ± 22.1	6308 ± 258	3.354	1.462
127a	9.80	2689 ± 61.6	871 ± 17.1	1319 ± 53.2	2304 ± 52.4	0.915	1.746
127b	2.20	324 ± 8.89	98.36 ± 1.34	193 ± 7.10	333 ± 16.3	0.647	1.729
129	10.20	20203 ± 853	1302 ± 58.6	1379 ± 61.7	1814 ± 37.9	4.536	1.315

UFZ 501, C2 concentration data in µg/kg (d = depth in meters)

d	2-EP	4-EP	3-EP	2.6-DMP	2.4-DMP	2.5-DMP	2.3-DMP	3.4-DMP	3.5-DMP
103	<4.20			<1.68					
105	10.6 ± 0.17	12.7 ± 0.25	9.39 ± 0.45	4.81 ± 0.09	15.60 ± 0.65	6.08 ± 0.19	3.46 ± 0.05	<1.68	<1.68
106	<4.20			4.14 ± 0.22	8.45 ± 0.39	<1.68	<1.68		
107				2.09 ± 0.12	5.59 ± 0.09				
108				3.21 ± 0.12	8.13 ± 0.08				
110	4.22 ± 0.20	8.04 ± 0.39	5.30 ± 0.17	6.66 ± 0.19	21.1 ± 1.11	2.45 ± 0.03	<1.68	8.01 ± 0.24	19.6 ± 0.22
113	<4.20	6.56 ± 0.18	5.72 ± 0.13	4.55 ± 0.17	10.1 ± 0.53	1.77 ± 0		4.59 ± 0.02	11.2 ± 0.13
115	<4.20			2.73 ± 0.11	7.38 ± 0.18	<1.68		2.94 ± 0.04	7.20 ± 0.06
116	<4.20	4.46 ± 0.18	5.40 ± 0.16	5.52 ± 0.06	12.4 ± 0.20	<1.68		5.57 ± 0.15	13.6 ± 0.02
117	12.8 ± 0.04	13.8 ± 0.09	20.2 ± 1.00	28.3 ± 1.45	51.8 ± 0.97	9.98 ± 0.42	8.43 ± 0.15	28.9 ± 0.36	70.9 ± 0.40
118	<4.20	5.28 ± 0.01	4.84 ± 0.16	3.87 ± 0.00	7.57 ± 0.40	1.73 ± 0.08	1.81 ± 0.05	4.24 ± 0.08	10.4 ± 0.02
119	29.9 ± 1.46	31.0 ± 0.87	52.4 ± 1.40	84.6 ± 3.63	147 ± 2.23	24.1 ± 0.39	24.5 ± 0.89	85.2 ± 1.15	209 ± 1.75
123	5.22 ± 0.02	5.05 ± 0.06	8.52 ± 0.08	5.48 ± 0.21	21.8 ± 0.28	5.47 ± 0.21	2.87 ± 0.09	11.4 ± 0.03	28.0 ± 0.18
124	8.23 ± 0.01	10.6 ± 0.03	8.83 ± 0.10	6.30 ± 0.02	21.8 ± 0.80	6.03 ± 0.29	3.22 ± 0.12	5.81 ± 0.15	14.2 ± 0.21
125	81.4 ± 2.07	236 ± 8.92	155 ± 2.86	49.4 ± 1.54	180 ± 3.39	83.5 ± 2.39	56.3 ± 2.42	74.8 ± 0.73	183 ± 3.02
126	299 ± 8.89	1320 ± 42.1	1667 ± 67.0	113 ± 5.40	575 ± 23.9	346 ± 1.63	286 ± 2.32	299 ± 1.99	733 ± 9.83
127a	158 ± 5.51	611 ± 13.5	887 ± 33.7	62.0 ± 1.79	340 ± 9.31	178 ± 2.68	130 ± 4.42	224 ± 1.78	549 ± 2.76
127b	20.2 ± 0.37	102 ± 1.12	149 ± 4.40	4.44 ± 0.17	49.3 ± 1.22	25.4 ± 0.84	19.0 ± 0.10	37.2 ± 0.12	91.1 ± 1.49
129	57.8 ± 1.62	248 ± 3.98	136 ± 5.15	26.8 ± 0.47	107 ± 2.39	81.4 ± 3.40	65.5 ± 3.32	54.5 ± 2.40	133 ± 3.01

UFZ 501, C3 concentration data in µg/kg and total SCAP (d = depth in meters)

d	2.4.6 TMP	2.3.6 TMP	2.3.5 TMP	3.4.5 TMP	2i-PP	2n-PP	4i-PP	3i-PP	4n-PP	total amount
103	1.08 ± 0.07	1.28 ± 0.07	4.87 ± 0.32	<0.96	<0.96	1.13	5.87	<0.96	<0.96	21.7 ± 0.65
105	2.39 ± 0.05	2.58 ± 0.17	8.96 ± 0.32	0.95 ± 0.05		2.88	12.01		3.69	119.0 ± 3.83
106	2.19 ± 0.13	2.26 ± 0.17	7.71 ± 0.50	1.12 ± 0.04		1.95	8.94		<0.96	52.8 ± 1.70
107	1.36 ± 0.06	1.29 ± 0.07	3.96 ± 0.17	<0.96		<0.96	3.11		<0.96	28.5 ± 0.72
108	1.54 ± 0.07	1.79 ± 0.11	8.09 ± 0.15	1.20 ± 0.05	1.52	4.06	21.97	<0.96	1.91	39.5 ± 0.87
110	2.62 ± 0.05	3.85 ± 0.09	17.2 ± 0.32	2.48 ± 0.04	<0.96	1.80	10.55		1.22	164.7 ± 5.76
113	1.73 ± 0.10	2.32 ± 0.16	9.66 ± 0.06	1.39 ± 0.02	<0.96	<0.96	5.09		<0.96	102.9 ± 8.22
115	1.81 ± 0.05	2.04 ± 0.10	5.51 ± 0.13	1.13 ± 0.02	1.20	2.41	12.34		<0.96	58.8 ± 6.80
116	2.74 ± 0.04	3.55 ± 0.11	10.9 ± 0.77	1.44 ± 0.07	5.00	11.27	75.97		10.27	103.3 ± 8.16
117	12.4 ± 0.84	19.4 ± 1.16	63.4 ± 1.68	2.78 ± 0.07	1.41	2.16	11.36		2.42	497.9 ± 24.3
118	2.60 ± 0.07	3.42 ± 0.11	7.09 ± 0.36	1.36 ± 0.10	9.45	40.73	210	1.97	34.29	93.7 ± 4.33
119	30.8 ± 1.53	51.8 ± 3.40	160 ± 0.19	17.3 ± 1.08	1.54	3.14	15.99	<0.96	3.01	1312.9 ± 25.0
123	4.93 ± 0.06	6.00 ± 0.33	25.9 ± 0.55	3.13 ± 0.12	2.43	3.30	12.18		3.91	193.5 ± 6.15
124	6.51 ± 0.30	4.93 ± 0.31	8.72 ± 0.07	1.40 ± 0.03	4.51	18.99	83.08	1.14	26.70	183.6 ± 4.64
125	22.1 ± 1.08	34.6 ± 2.18	98.9 ± 2.51	15.1 ± 0.49	9.71	67.93	284	<0.96	111	1836.4 ± 51.4
126	15.8 ± 1.17	20.1 ± 0.53	93.4 ± 2.32	32.4 ± 0.47	6.65	42.62	199	1.20	62.45	20734.4 ± 593
127a	13.3 ± 0.27	18.8 ± 0.69	157 ± 10.0	26.0 ± 0.31	1.10	4.47	14.94	<0.96	6.40	7848.1 ± 271
127b	1.63 ± 0.06	1.77 ± 0.03	26.2 ± 1.46	3.83 ± 0.01	<0.96	1.13	5.87		<0.96	1466.6 ± 45.1
129	1.28 ± 0.05	2.44 ± 0.17	5.61 ± 0.39	4.03 ± 0.02	<0.96	2.88	12.01		3.69	5444.7 ± 1038

UFZ 601, water content, C0 - C1 concentration data in µg/kg, PCF and MPR

depth in m	H_2O in %	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	MPR
180	2.18	9480 ± 117	1340 ± 61	2420 ± 46	2630 ± 98	0.825	1.087
181	1.15	293 ± 1.9	59.5 ± 1.8	60.2 ± 1.9	141 ± 0.1	0.531	2.342
183	2.73	398 ± 18	118 ± 0.2	135 ± 4.5	269 ± 6.9	0.538	1.993
184.5	0.14	138 ± 5.9	60.4 ± 0.8	49.1 ± 2.3	69.7 ± 1.6	0.454	1.420
186	1.74	286 ± 9.5	163 ± 5.7	132 ± 5.5	179 ± 2.3	0.438	1.356
187	1.29	318 ± 16	186 ± 7.1	252 ± 5.9	401 ± 19	0.676	1.591
188	0.57	185 ± 0.7	186 ± 4.6	340 ± 8.2	753 ± 17	0.507	2.215
189	3.00	761 ± 2.2	629 ± 29	1190 ± 45	2220 ± 77	0.626	1.866
190	12.9	13100 ± 280	2330 ± 61	3550 ± 12	6080 ± 158	0.894	1.713
191	10.5	7720 ± 3.9	827 ± 27	1289 ± 56	2190 ± 0.3	0.944	1.699
192	11.8	< 35.4	<2.52				

UFZ 601, C2 concentration data in µg/kg (d = depth in meters)

d	2-EP	4-EP	3-EP	2.6-DMP	2.4-DMP	2.5-DMP	2.3-DMP	3.4-DMP	3.5-DMP
180	255 ± 12	963 ± 10	454 ± 18	37 ± 0.7	345 ± 13	279 ± 7.9	238 ± 8.8	289 ± 2.1	404 ± 17
181	52 ± 0.7	75 ± 0.1	100 ± 4.0	13 ± 0.6	44.1 ± 0.8	34 ± 0.6	26 ± 0.4	16 ± 0.6	92 ± 1.5
183	94 ± 1.1	115 ± 2.7	176 ± 7.3	18 ± 0.4	58.4 ± 1.4	61 ± 2.1	42 ± 0.5	32 ± 0.9	142 ± 4.2
184.5	52 ± 2.3	49 ± 0.6	70 ± 3.1	25 ± 0.3	80.3 ± 2.3	48 ± 1.5	30 ± 1.1	<1.68	94 ± 2.3
186	100 ± 2.3	97 ± 0.1	36 ± 1.2	51 ± 1.3	155 ± 6.5	106 ± 0.1	64 ± 2.9	25 ± 0.9	198 ± 8.6
187	58 ± 2.1	162 ± 2.4	193 ± 1.1	28 ± 0.5	96.1 ± 1.2	65 ± 1.7	45 ± 1.9	35 ± 1.5	116 ± 4.4
188	84 ± 1.5	219 ± 3.3	399 ± 7.8	38 ± 0.8	125 ± 0.4	90 ± 1.1	78 ± 3.4	81 ± 0.3	177 ± 0.7
189	159 ± 6.7	567 ± 27	748 ± 4.6	69 ± 3.1	250 ± 4.2	186 ± 3.4	144 ± 1.8	128 ± 3.4	409 ± 3.6
190	141 ± 5.7	671 ± 25	779 ± 32	40 ± 0.8	217 ± 1.4	186 ± 5.9	149 ± 1.7	<1.68	641 ± 23
191	37 ± 0.8	181 ± 0.7	141 ± 4.1	9.3 ± 0.4	52.4 ± 0.9	49 ± 0.5	42 ± 0.2		172 ± 7.4
192	<4.20			<1.68					

UFZ 601, C3 concentration data in µg/kg and total SCAP (d = depth in meters), no propylphenols are present

d	2.4.6 TMP	2.3.6 TMP	2.3.5 TMP	3.4.5 TMP	total amount
180	8.1 ± 0.1	9.9 ± 0.4	57 ± 2.1	25 ± 0.2	19234 ± 414.4
181	1.3 ± 0	1.9 ± 0.1	35 ± 1.7	< 0.96	1044 ± 16.9
183	1.3 ± 0.1	2.4 ± 0.1	47 ± 1.5		1709 ± 51.4
184.5	5.1 ± 0.2	7.4 ± 0.3	59 ± 0.4		699 ± 24.7
186	8.2 ± 0.2	11.3 ± 0.2	113 ± 1.2	11 ± 0.3	1735 ± 48.1
187	4.2 ± 0	5.6 ± 0.1	59 ± 2.9	5 ± 0.2	1711 ± 67.5
188	6.7 ± 0	12.6 ± 0.4	106 ± 3.4	7.6 ± 0.1	2889 ± 53.8
189	3.2 ± 0	5.3 ± 0	185 ± 5.6	12 ± 0.2	7665 ± 217.0
190	< 0.96		152 ± 7.5	< 0.96	28036 ± 613.5
191			26 ± 0.7		12736 ± 103.4
192	< 0.96				

Appendix II

- **SCAP data on gasworks site**

Sampling 14.11.2001, µg/L, no propylphenols present at the site

OW	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	MPR	P.Index	Total SCAP
B6	15.3 ± 0.9	2.50 ± 0.2	1.60 ± 0.14	0.70 ± 0.02	0.65	0.43	60	33.7 ± 1.1
B7	< 8.85	75.0 ± 1.2	7.40 ± 0.26	12.3 ± 0.42	0.09	1.66	500	1130 ± 52
B8		1.00 ± 0.1	< 0.63	< 0.63	0.01		130	204 ± 9.4
B9		12.5 ± 0.2			0.02		460	771 ± 33.1
B10		4.00 ± 0.1			0.07		180	66.8 ± 2.4
B11		16.9 ± 0.2			0.06		320	326 ± 12.6
B12		28.0 ± 0.5	0.61 ± 0.03	3.10 ± 0.13	0.21	5.08	120	164 ± 7.4
G2	61.3 ± 4.2	644 ± 12	112 ± 5.1	244 ± 5.5	0.27	2.01	12520	4270 ± 145
G7	272 ± 4.1	495 ± 18	0.61 ± 0.02	199 ± 3.9	0.45	326	1660	2350 ± 104
G12	< 8.85	< 0.63					30	7.70 ± 2.3
G16							10	

OW	2-EP	4-EP	3-EP	2.6-DMP	2.4-DMP	2.5-DMP	2.3-DMP	3.4-DMP	3.5-DMP
B6	3.50 ± 0.1	< 1.05	< 1.05	0.90 ± 0.1	2.20 ± 0.1	2.80 ± 0.2	2.80 ± 0.2	< 0.42	1.40 ± 0.1
B7	22.3 ± 1.1			108 ± 2.3	179 ± 3.5	131 ± 3.2	47.5 ± 1.7		254 ± 11
B8	1.00 ± 0.1			75.0 ± 2.4	1.80 ± 0.1	6.00 ± 0.3	1.30 ± 0.1		17.8 ± 0.4
B9	34.5 ± 12			128 ± 3.2	87.1 ± 2.8	105 ± 2.8	42.4 ± 0.6		246 ± 9.8
B10	1.50 ± 0.1			3.50 ± 0.1	7.50 ± 0.2	4.60 ± 0.2	2.80 ± 0.2		16.0 ± 0.4
B11	6.10 ± 0.3			20.0 ± 0.5	39.0 ± 1.2	22.0 ± 0.3	10.4 ± 0.3		69.7 ± 1.1
B12	4.60 ± 0.2			12.5 ± 0.2	22.1 ± 0.3	21.8 ± 0.3	7.90 ± 0.3		39.9 ± 1.8
G2	110 ± 3.2			288 ± 11	644 ± 25	580 ± 27	231 ± 11		1060 ± 23
G7	59.4 ± 2.1			163 ± 4.6	78.6 ± 2.1	327 ± 14	126 ± 6.4		420 ± 17
G12	< 1.05			7.70 ± 0.1	< 0.42				
G16				< 0.42					

OW	2.4.6 TMP	2.3.6 TMP	2.3.5 TMP	3.4.5 TMP
B6	< 0.24			
B7	146 ± 5.2	62.6 ± 2.9	87.2 ± 2.7	< 0.24
B8	59.9 ± 2.7	24.6 ± 1.1	8.90 ± 0.3	6.30 ± 0.2
B9	45.8 ± 2.2	28.9 ± 1.2	40.9 ± 2.1	< 0.24
B10	7.00 ± 0.2	3.40 ± 0.1	11.3 ± 0.3	5.20 ± 0.2
B11	62.7 ± 3.1	27.9 ± 1.1	51.4 ± 2.5	< 0.24
B12	9.00 ± 0.03	5.30 ± 0,2	10.0 ± 0.2	
G2	148 ± 6.2	53.6 ± 1.7	94.2 ± 4.2	
G7	85.6 ± 3.9	49.2 ± 2.2	72.8 ± 3.1	
G12	< 0.24			
G16				

Sampling 17.01.2002, µg/L, no propylphenols present at the site

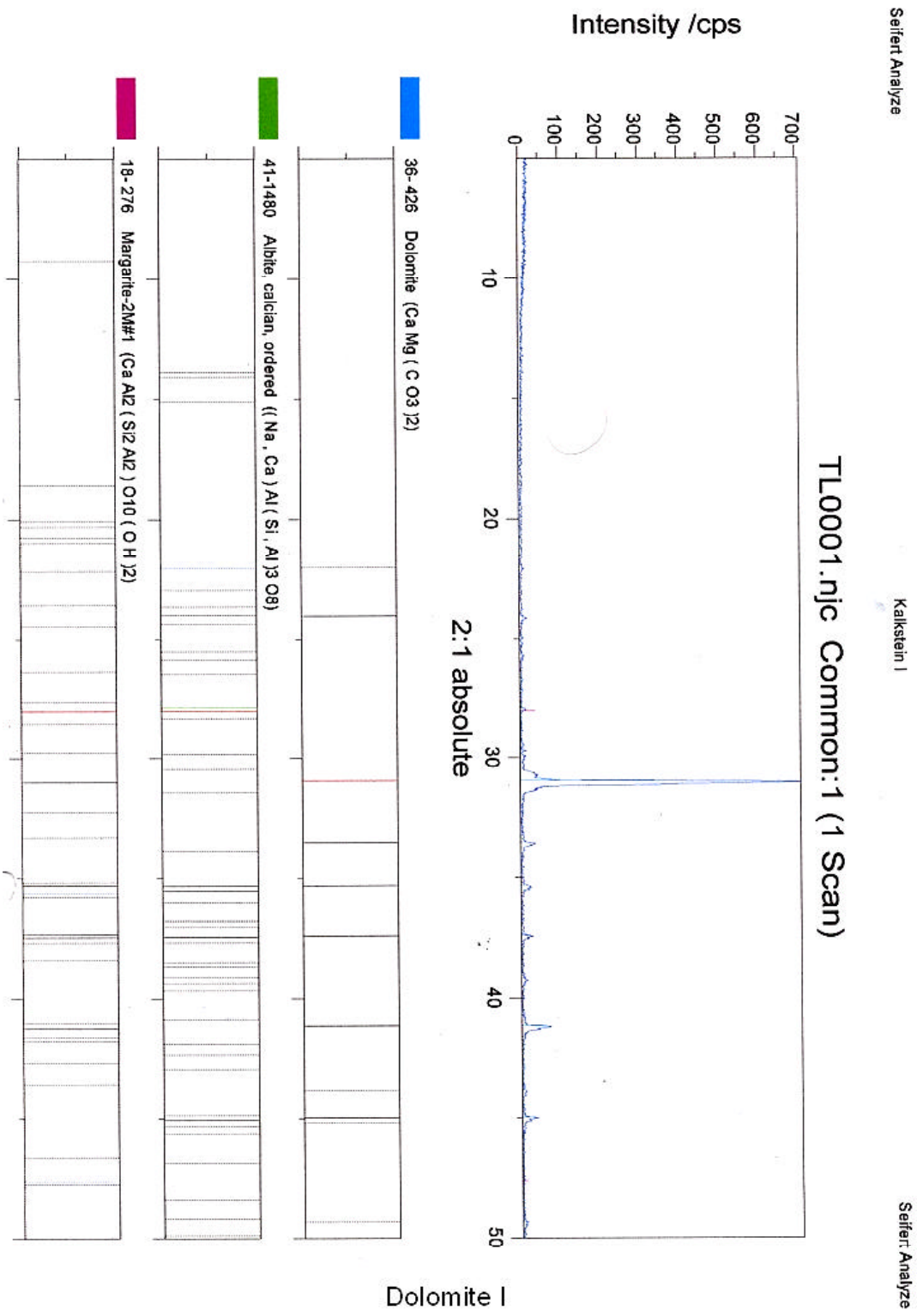
OW	Phenol	o-Cresol	p-Cresol	m-Cresol	PCF	MPR	P.Index	Total SCAP
B6	< 8.85	< 0.63			0		10	37.70 ± 1.1
B7		142 ± 5.2	36.8 ± 1.6	47.8 ± 1.9	0.47	1.5	820	511.9 ± 22
B8		5.60 ± 0.1	< 0.63	< 0.63	0.01		250	429.3 ± 9.4
B9		48.6 ± 2.1			0.23		180	232.8 ± 8.1
B10	37.1 ± 1.2	85.6 ± 3.7	17.6 ± 0.5	30.7 ± 0.9	0.30	2	530	637.3 ± 16.4
B11		< 0.63					80	
B12							20	
G2		10.8 ± 0.4	< 0.63		0.23		240	52.70 ± 1.4
G7	1442 ± 34.1	4891 ± 145	356 ± 14.5	2339 ± 24	0.55	6	11470	19520 ± 504
G12	< 8.85	< 0.63					60	17.6 ± 0.3

OW	2-EP	4-EP	3-EP	2.6-DMP	2.4-DMP	2.5-DMP	2.3-DMP	3.4-DMP	3.5-DMP
B6	< 1.05		2.10 ± 0	9.10 ± 0.2	2.80 ± 0.1	5.10 ± 0.2	1.40 ± 0.1	1.10 ± 0	6.30 ± 0.2
B7	21.0 ± 1.0	6.60 ± 0.2	18.5 ± 1	6.50 ± 0.2	38.4 ± 1.2	35.6 ± 1.2	14.4 ± 0.7	26.1 ± 0	104 ± 5.2
B8	10.3 ± 0.4	< 1.05	1.00 ± 0	62.1 ± 2.8	8.00 ± 0.2	27.7 ± 1.3	5.60 ± 0.3	215 ± 3	28.6 ± 0.9
B9	4.10 ± 0.1		3.20 ± 0	26.2 ± 1.1	30.5 ± 1.3	32.0 ± 1.2	12.3 ± 0.4	7.60 ± 0	44.9 ± 1.4
B10	14.8 ± 0.9	8.50 ± 0.3	20.5 ± 1	32.2 ± 1.3	66.9 ± 2.1	44.9 ± 1.9	22.3 ± 0.9	197 ± 2	< 0.42
B11	< 1.05			< 0.42					
B12									
G2	2.60 ± 0.1	0.70 ± 0.1	2.40 ± 0	3.10 ± 0.1	7.90 ± 0.3	6.90 ± 0.2	2.40 ± 0.1	< 0.42	11.0 ± 0.4
G7	405 ± 14	214 ± 8.1	944 ± 9	1270 ± 52	270 ± 8.1	2549 ± 61	964 ± 17		2155 ± 19
G12	< 1.05			17.9 ± 1.2	< 0.42				

OW	2.4.6 TMP	2.3.6 TMP	2.3.5 TMP	3.4.5 TMP
B6	4.00 ± 0.19	2.30 ± 0.11	2.80 ± 0.12	0.70 ± 0.10
B7	4.50 ± 0.22	1.10 ± 0.10	6.40 ± 0.25	2.10 ± 0.11
B8	34.6 ± 1.62	14.3 ± 0.71	11.3 ± 0.41	5.50 ± 0.23
B9	5.20 ± 0.24	4.00 ± 0.16	10.4 ± 0.24	3.20 ± 0.12
B10	21.6 ± 1.13	12.6 ± 0.54	8.90 ± 0.32	16.5 ± 0.78
B11	< 0.24			
B12				
G2	1.40 ± 0.10	0.70 ± 0.10	2.00 ± 0.10	0.80 ± 0.10
G7	671 ± 31.7	341 ± 17.5	556 ± 27.6	154 ± 11.5
G12	< 0.24			

Appendix III

- **XRD**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500
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300
200
100
0
10
20
30
40
50
2:1 absolute
TL0001.njc Common:1 (1 Scan)
Kalkstein I
Seifert Analyze
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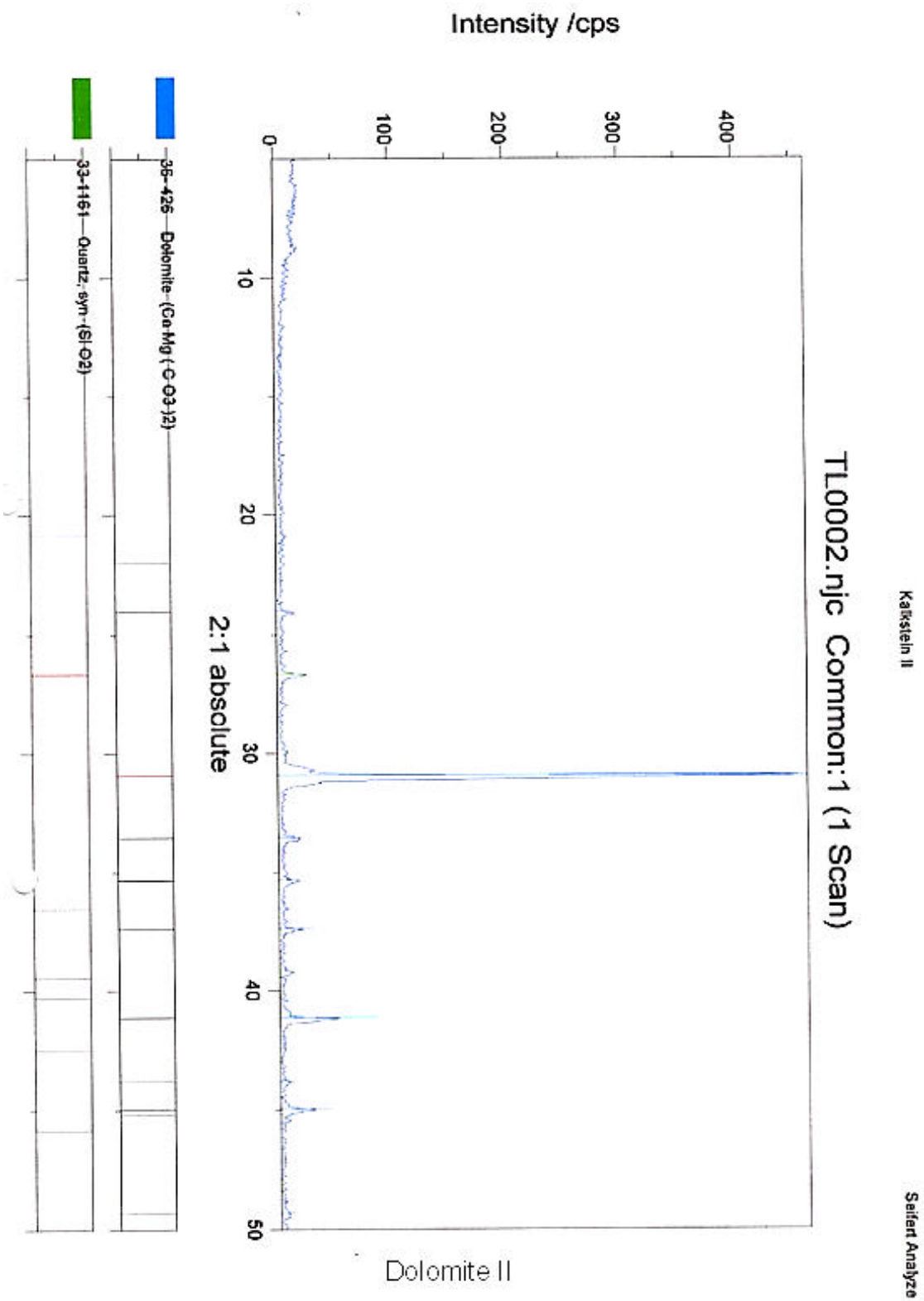
41-1480 Albite, calcian, ordered ((Na , Ca) Al (Si , Al)3 O8)
18-276 Margarite-2M#1 (Ca Al2 (Si2 Al2) O10 (O H)2)
Dolomite I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100
200
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400
10
20
30
40
50
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2:1 absolute
Dolomite II
Kalkstein II
Seifert Analyze
35-426 Dolomite, (Ca Mg (C O3)2)
33-1161 Quartz, syn (Si O2)

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Curriculum Vitae

1999-2002	Ph.D, Friedrich Schiller Universität Jena
1998-1999	Research Assistant, University College London
1997-1998	M.Sc. Hydrogeology, University College London
1991-1997	Diplom-Chemiker, Universität Leipzig
1994-1995	Erasmus Student in Chemistry at Dublin City University
1991	A-Level

Eidestattliche Erklärung

Hiermit erkläre ich, daß ich die hier vorliegende Dissertationsschrift in selbständiger Arbeit und nur unter Zuhilfenahme der Angegebenen Quellen angefertigt habe.

Jena, 14.11.2002