Polycyclic Aromatic Hydrocarbons (PAHs) in River bank soils

Source identification and a risk assessment

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Was wir wissen, ist ein Tropfen,
Was wir nicht wissen, ein Ozean

(Isaac Newton)

Erklärung:
Hiermit versichere ich gemäß §11 (3) der Promotionsordnung vom 30. April 1990, dass ich diese als Dissertation vorgelegte Arbeit selbstständig angefertigt und alle benutzten Hilfsmittel in der Arbeit angegeben habe. Sie ist weder als Prüfungsarbeit für eine andere Prüfung noch ganz oder teilweise als Dissertation an einer anderen Fakultät oder einem anderen Fachbereich eingereicht worden.

Mainz, den

(Carmen Pies)

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and found in the atmosphere, aquatic environment, sediments and soils. For environmental risk assessments and the allocation of the polluter it is important to know the PAH sources.

PAH contamination sites are usually the result of anthropogenic processes. Three major sources are known: i) petroleum, including crude oil and its refined products and coals (petrogenic PAHs), ii) burning of organic matter (pyrogenic PAHs) and iii) transformation products of natural organic precursors present in the environment (diagenetic processes). PAH contamination sites, which are influenced by almost all these anthropogenic processes are often river bank soils.

In one case elevated PAH concentrations were found in river bank soils when building a retention area along the Mosel River. The source of the PAHs in this area was unclear and required the investigation of possible sources. To evaluate the PAH distribution along the Mosel River, a section of ~ 160 km along the river and a short section along the Saar River were investigated within this study. Concentrations of the Σ_{16} EPA PAHs were as high as 81 mg kg^{-1} dry weight (dw). Additionally, coal particles were identified in some soils, which originated from mining activities in the Saarland region. PAH distribution patterns of the sixteen EPA PAHs suggest a mainly pyrogenic origin and in some cases a mixture of pyrogenic and petrogenic origin. For further source identifications a more detailed investigation was recommended and performed.

Thus, five sampling sites were selected for a comprehensive investigation of PAH sources. Two sites were located before the confluence of the Mosel and Saar River, one site at the confluence and two sites after the confluence. The examination included typical forensic methods such as PAH distribution patterns of 45 PAHs (including alkylated PAHs), calculation of PAH ratios, determination of PAH alkyl homologues, n-alkanes, principal component analysis (PCA) and coal petrography. The results revealed a mainly pyrogenic source at sampling sites before the confluence of the two rivers, and at one site an input of lubricating oil could be detected. At and after the confluence, a mixture of pyrogenic and petrogenic inputs

were present. With the help of coal petrography, coal derived particles could be identified in these soils. Therefore, coal was suggested to be the petrogenic source. It could be shown that sites with diffuse sources of contaminants, like the bank soils of the Mosel River, are difficult to characterize. Source identification of complex PAH mixtures requires more than one identification method to identify PAH source(s). Hence, a concept for source identification of bank soils could be proposed: 1) collection of information about site history, 2) use of coal petrography if the samples are impacted by coal mining 3) selection and use of alkylated PAHs (i.e. methylnaphthalenes, methylphenanthrenes -anthracenes, methylfluoranthenes -pyrenes) with respect to distribution patterns and a calculation of PAH ratios, 4) interpretation of n-alkane measurements, 5) use of C_1-C_4 homologue series if data are available and 6) use of PCA.

As previously mentioned for detailed source identifications, the use of various forensic methods is essential. Determination of PAH alkyl homologue series, biomarkers and isotopes are often recommended. However, these methods are complex and expensive. Therefore, source identification was evaluated using three different methods (i.e. PAH distribution patterns of an extended PAH spectrum, PAH ratios and analyses of n-alkanes). It was assessed if these methods were sufficient for the initial steps in identifying sources of PAHs in selected samples, and if they could be used for decision-making purposes before resorting to more expensive methods. Point- and non-point sources were identified by applying the three methods and it could be shown that these relatively simple methods are sufficient in determining the primary source of the investigated samples, and to help direct further analytical steps.

In a last step of this study two soils (one before the confluence of the Mosel and Saar rivers and one after the confluence), and one sediment of the Mosel River were evaluated by investigating the mutagenic potential of the soils and the sediment with a fluctuation version of the Ames-test.
The study showed that coal bearing soils at the Mosel River do not exhibit a greater mutagenic potential than other soils or sediments without coal particles.

Zusammenfassung

Polyzyklische aromatische Kohlenwasserstoffe (PAK) sind weltweit allgegenwärtig und treten in der Atmosphäre, in wässrigen Systemen, Sedimenten und Böden auf. Es ist wichtig die Quelle der PAK zu kennen, um eine Abschätzung des Umweltrisikos vornehmen und die Kontamination einem Verursacher zuordnen zu können. PAK Kontaminationen gehen meist aus anthropogenen Prozessen hervor. Drei Hauptkontaminationsquellen sind bekannt: 1) Petroleum (Rohöl mit seinen raffinierierten Produkten und Kohle – petrogene PAK), 2) Verbrennung von organischem Material (pyrogene PAK) und 3) Transformationsprodukte von natürlichen organischen Vorläufersubstanzen (aus diagenetischen Prozessen). Zu den PAK kontaminierten Gebieten, die fast von all diesen anthropogenen Prozessen beeinflusst sind, zählen oft Uferböden.

Zum Beispiel wurden während Baumaßnahmen zum Bau einer Retentionsfläche an der Mosel erhöhte PAK Konzentrationen im Uferboden festgestellt, und die Herkunft dieser blieb unbekannt. Aus diesem Grund wurde die PAK Verteilung entlang der Mosel auf einer Strecke von ca. 160 km und zum Teil auch an der Saar untersucht. In dieser Untersuchung reichten die gemessenen Gehalte der Summe der sixteen EPA PAK zum Teil bis zu 81 mg kg^{-1}. Zusätzlich konnten Kohlepartikel, die aus dem Kohlebergbau des Saarlandes stammen, in manchen Böden identifiziert werden. Die Verteilungsmuster der PAK weisen zumeist auf eine pyrogene Quelle hin, in manchen Proben kann aber auch eine Mischung aus pyrogenen und petrogenen PAK beobachtet werden. Zur Bestimmung der genauen PAK Herkunft werden allerdings mehrere Untersuchungen benötigt und wurden im weiteren Verlauf dieser Studie durchgeführt.

Dafür wurden fünf Standorte entlang der Mosel bzw. Saar für eine detaillierte Untersuchung zur Herkunft der PAK ausgewählt. Zwei Standorte befanden sich vor der Saarmündung, ein Standort an der Saarmündung und zwei Standorte hinter der Saarmündung. Zu den durchgeführten Untersuchungen zählten typische forensische Methoden wie zum Beispiel PAK Verteilungsmuster von 45 PAK (darunter auch alkylierte PAK), die Berechnung von PAK Verhältnissen, die Bestimmung von PAK Alkyl-Homologen, n-Alkanen, eine Hauptkomponenten-Analyse und

Kohlepetrographie. Die Ergebnisse zeigten, dass die PAK in Böden vor der Saarmündung hauptsächlich pyrogener Herkunft sind. Es konnte aber in einem Boden auch ein Eintrag von Schmierölen beobachtet werden. In Böden an und nach der Saarmündung wurde eine Mischung aus pyrogenen und petrogenen PAK festgestellt. Mit Hilfe von Kohlepetrographie konnten Kohle- und kohlebürtige Partikel nachgewiesen werden. Aus diesem Grund kann angenommen werden, dass Kohle die petrogene Quelle in den Böden an und nach der Saarmündung darstellt. Es konnte auch gezeigt werden, dass eine diffuse Quelle von PAK, so wie sie an der Mosel vorzufinden ist, schwer zu charakterisieren ist. Deshalb ist es bei komplexen PAK Kontaminationen notwendig, mehr als nur eine PAK Identifizierungsmethode anzuwenden. Folgendes Konzept wird daher vorgeschlagen: 1) Beschaffung von Informationen über die Standorthistorie, 2) Anwendung von Kohlepetrographie, wenn die Proben vom Bergbau beeinflusst sind, 3) Auswahl an alkylierten PAK treffen (d.h. Methylnaphthaline, Methylphenanthrene -anthracene und Methylfluoranthene – pyrene) im Hinblick auf PAK Verteilungen und die Berechnung von PAK Verhältnissen, 4) Interpretation von n-Alkan Messungen, 5) Auswertung von C_1-C_4 PAK Homologen soweit dies möglich ist und 6) Anwendung einer Hauptkomponentenanalyse.

Wie schon zuvor erwähnt sind verschiedene forensische Methoden zur Herkunftsbestimmung von PAK erforderlich. Die Bestimmung von PAK Alkylhomologen, Biomarkern und Isotopen wird oft empfohlen ist aber sehr komplex und teuer. Zu diesem Zweck wurde getestet ob drei Methoden (PAK Verteilungsmuster eines erweiterten PAK Spektrums, Berechnung von PAK Verhältnissen und n-Alkan Analysen) ausreichend sind, um eine Quellidentifizierung vornehmen zu können, bevor komplexe und teure Methoden zur Anwendung kommen. Es wurden hierzu Punkt- und diffuse PAK Quellen untersucht und es konnte gezeigt werden, dass drei relativ einfache Methoden ausreichend sind, um eine Abschätzung der PAK Herkunft geben zu können. Außerdem vereinfachen sie die Entscheidung zur Notwendigkeit von weiteren detaillierten, komplexeren Analysen bzw. Methoden.

Im letzten Schritt dieser Studie wurden zwei Böden (ein Uferboden der Mosel vor der Saarmündung und ein Boden der Mosel nach der Saarmündung) und ein Sediment

der Mosel mit Hilfe des Ames-Fluktuations Test auf ihr mutagenes Potential untersucht. Die Untersuchungen ergaben, dass die kohlehaltigen Böden kein größeres mutagenes Potential aufzeigen als die Böden ohne Kohlepartikel.

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…….

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…….

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Chapter 2: **Pies, C., Yang, Y., Hofmann, T. (2007)**.
"Coal mining activities and the distribution of polycyclic aromatic hydrocarbons (PAHs) in floodplain soils of the Mosel and Saar River." J. Soil Sediment 7(4): 216-222.

Chapter 3: **Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T. (2008)**.
"Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils." Chemosphere 72: 1594-1601.

Chapter 4: **Pies, C., Ternes, T.A., Hofmann, T. (2008):**
“Identifying sources of polycyclic aromatic hydrocarbons (PAHs) in soils: Distinguishing point and non-point sources using an extended PAH spectrum and n-alkanes.” J. Soil Sediment 8, 312-322.

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Achten, C., Yang, Y., Pies, C., Ternes, T., Hofmann, T.:
“Environmental Impact of Polycyclic Aromatic Hydrocarbons (PAHs) in Coal Particles on Sediment Quality”

Contents

1 General Introduction

1.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are an ubiquitous class of contaminants due to atmospheric and aquatic circulation (Laflamme and Hites 1978). They are persistent and consist of more than 100 individual compounds and 30 – 40 exhibit environmental relevance. However, only sixteen are defined as “priority pollutants” by the US Environmental Protection Agency (US EPA), and thus are routinely analyzed. Since the industrial revolution, the PAH concentrations in the environment have been continuously increasing (Grope 2001; Gschwend and Hites 1981; Pereira et al. 1999; Wakeham et al. 1980a). However, since 1980 there has been a slight decrease in the concentrations of these pollutants found in Europe (Fernández et al. 2000).

PAHs occur in high structural diversity and complex mixtures and the hydrocarbon mixtures in different source materials vary in the relative contribution of their individual components (Neff et al. 2005). PAH contaminations are mainly caused by anthropogenic processes. Three major sources are known: i) petroleum, including crude oil and its refined products and coals (petrogenic PAHs), ii) burning of organic matter (pyrogenic PAHs) and iii) transformation products of natural organic precursors present in the environment (diagenetic processes) (Neff 1979). A potential fourth source are biogenic PAHs, i.e. formed from fungi, bacteria, plants or animals in a sedimentary environment. That means no diagenetic processes have contributed to PAH formation. Attempts to produce biogenic PAHs have failed and hence biogenic PAHs seem to be of no significance and are negligible (Neff 1979).

In general, PAHs reach soils and the aquatic environment by an atmospheric deposition, through the discharging of industrial and domestic sewage effluents, surface runoff, airborne particulates and spillages of petroleum products (Neff 1979). They can be produced naturally (e.g. by volcanoes, forest fires, diagenesis of organic matter) or by anthropogenic processes (e.g. vehicle emissions, industry, households, leaching oil tanks), in which the anthropogenic PAH inputs usually dominate the natural PAH inputs.

PAHs are nonpolar organic chemicals with low water solubilities (i.e. high K_{ow} values). Hence, PAHs especially high molecular PAHs exhibit a great affinity to adsorb to particles such as soot and to organic matter such as humic substances or coal and accumulate in soils and sediments (Neff et al. 2005; Youngblood and Blumer 1975).

Adsorption is a process where molecules attach to a two-dimensional surface. It is generally restricted to a surface or interface (e.g. solid/liquid; solid/gas; liquid/gas). In contrast, absorption is a process where a molecule penetrates into a three-dimensional matrix (Schwarzenbach et al. 2003). Due to the heterogeneous nature of soils, both processes may take place simultaneously, and can not be separated from each other experimentally (Yang 2007).

PAH concentrations in soils and sediments may have a factor of 1000 or more than in the surrounding pore water or overlying water column (Notar et al. 2001). Once accumulated in soils or sediments dissipation pathways may be volatilization, irreversible sorption, leaching and biodegradation (Trapido 1999). Hence, soils or sediments can act as a sink, but also as a source of PAHs. Therefore, these soil and sediment bound PAHs may present a potential risk to the aquatic and terrestrial environment. In contrast low molecular PAHs are predominantly present in the vapor phase and may enter the environment from rainfall or dry fallout (Neff et al. 2005).

The mobility of PAHs greatly affects the bioavailability. PAH desorption to surface and pore water influences the availability for biological uptake, and with increasing K_{ow} values (i.e. increasing molecular weight) the bioavailability of PAHs decreases (Brenner et al. 2002). Hence, low molecular weight PAHs are more bioavailable than high molecular weight PAHs. However, pyrogenic PAHs are assumed to be less bioavailable than petrogenic PAHs due to their strong association with combustion particles such as soot (Gustafsson et al. 1997).

The predominant occurrence of PAHs is found near urban centers (Laflamme and Hites 1978). Due to atmospheric transport they also occur in arctic regions (Dahle et al. 2003; Yunker and MacDonald 1995), in sediments of high altitude lakes (Fernández et al. 1999; Grimalt et al. 2004) and in deep-sea sediments (Ohkouchi et al. 1999).

Most of the studies to elucidate PAH sources are dealing with sediments, suspended matter and aerosols (Benlahcen et al. 1997; Brenner et al. 2002; Deng et al. 2006; Rehwagen et al. 2005) while bank soils are rarely investigated. However, bank soils (i.e. floodplain soils) are a sink for pollutants like PAHs, other organic contaminants and heavy metals (Götz et al. 2007; Hensel et al. 2006; Krüger et al. 2005; Gocht et al. 2001; Witter et al. 1998). Malmon et al. (2002) showed that floodplain sedimentation and erosion processes, which are mainly caused by floods, can influence the redistribution of anthropogenic contaminants. Therefore, beside atmospheric inputs of pollutants (e.g. PAHs), flood events strongly affect floodplain soil contamination. A study by Hilscherova et al. (2007) showed that PAHs in floodplain soils exhibit long-term contamination. The authors also showed that floods served as a vector of PAH contamination from sediments to soil. Witter et al. (2003) investigated depth profiles of floodplain soils of the Elbe River and found PAH contamination and other organic contaminants such as hexachlorobencene (HCB), dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyl (PCB) in several depths. They concluded the contamination was associated with flood events. Therefore, flood events represent an important contamination pathway for river bank soils. Unfortunately, most studies focus on river bed sediments and suspended matter. The importance to include floodplain soils for a comprehensive risk assessment was shown by Hilscherova et al. (2007).

1.2 Source identification of PAHs

Due to increasing environmental awareness contaminated sites are often required to be remediated. However, the responsible parties have to be found, and environmental forensic methods provide a way of determining who is responsible for the contamination. Due to the toxic relevance of PAHs for forensic reasons, an appropriate risk management is crucial to identify their sources.

To examine the source of PAH contaminations several methods can be applied and are described in the following.

To characterize PAH containing samples, previous studies have used forensic methods including total ion chromatograms, n-alkanes, PAHs (with PAH alkyl homologue series), biomarkers such as isoalkanes and isoprenoids, steranes and terpanes, principal component analysis, high volatile compounds, dye and other fuel additives, stable isotope ratios, and aliphatic as well as aromatic fractions to distinguish several raw materials, i.e. point sources such as crude oil, coals, etc. (Barrick et al. 1984; Brown et al. 2006; Kaplan et al. 1997; Kaplan et al. 2001; Marr et al. 1999; Murphy and Brown 2005; Radke et al. 1984; Sandercock and Du Pasquier 2003; Wang and Fingas 2003). Other studies have investigated PAH contaminated soils (Costa et al. 2004; Saber et al. 2006; Stout and Wasielewski 2004), sediments (Costa et al. 2004; Saber et al. 2006) and water (Costa et al. 2004) located near former industrial companies (i.e., point sources, but in an environmental matrix) using aforementioned forensic methods. PAH containing atmospheric particles from wood smoke (Dos Santos Barbosa et al. 2006), coal smoke (Dos Santos Barbosa et al. 2006; Oros and Simoneit 2000; Reddy et al. 2003; Wornat et al. 2001) household soot (Reddy et al. 2003) and urban particulate matter (Purificación López et al. 2003; Sharma and McBean 2001) were also characterized (i.e., atmospheric point sources).

For distinguishing between petrogenic and pyrogenic sources, PAH ratios of selected compounds are commonly used such as the ratios of phenanthrene/anthracene and fluoranthene/pyrene. In addition, the ratios of substituted and unsubstituted PAHs are crucial for source identification as well as PAH distribution patterns considering the relative concentration of each single PAH. Low molecular weight PAHs with only two or three fused benzene rings as well as alkylated homologues are major constituents of petroleum (Fernandes et al. 1997), while substituted PAHs are more abundant than unsubstituted PAHs (Sporstöl et al. 1983; Stout et al. 2002a). Furthermore, homologues with two to three alkyl carbons are usually more abundant than homologues with more than three alkyl moieties, and thus the distribution of alkyl PAHs shows a bell shaped characteristic with respect to the degree of alkylation. In general, high molecular weight PAHs with four to six rings are generated mainly by incomplete combustion of organic matter, inferring pyrogenic PAHs (e.g. fluoranthene, pyrene, benzo(ghi)perylene) (Fernandes et al. 1997). They are often

abundant in vapor and particulate phases of engine exhaust, whereas two to three ring PAHs are predominantly in the vapor phase and four to six ring PAHs are associated with particulate phases (e.g. soot). In pyrogenic sources the dominant PAHs of each homologue series (C_1-C_4 PAH homologues) are unsubstituted PAHs or a homologue with only one or two alkyl substitutes. This produces a decreasing concentration in the distribution within the homologue series (C_0>C_1>C_2>C_3>C_4) (Sporstöl et al. 1983; Stout et al. 2002a).

Comparing the distribution of n-alkanes with odd and even carbon numbers is helpful to detect oil and fuel sources such as hydraulic or lubricating oils and diesel or gasoline. Therefore, the carbon preference index (CPI) is used, providing information about biogenic/terrestrial and petroleum inputs as well as pristane/phytane ratios and the n-alkane pattern (Colombo et al. 1989; Stout et al. 2001; Tolosa et al. 2004; Wu et al. 2007; Yunker and Macdonald 2003).

Furthermore, exploratory statistical methods in the form of principal component analysis are applied. With this method a high information density is reduced to its most important or “principal” components. Additionally, the method permits the visualization of results, thus representing the general difference between samples (Jackson 1991).

In case of coal mining impacted areas it is of particular importance to include coal petrography. This optical method enables the observation, identification, classification and quantification of heterogeneous organic matter in soils and sediments, especially coal and coal derived particles (Ligouis et al. 2005; Yang 2007; Yang et al. 2008a; Yang et al. 2008b), which could be the main geosorbents for PAHs (Yang et al. 2008c).

1.2.1 PAHs in coals

Peat, generally formed by debris of land plants, is converted to coal by undergoing geochemical processes such as temperature and pressure over hundred millions of

years. First lignite is formed and thereafter, with increasing coalification, bituminous coal, anthracite and at last graphite. Coal is composed of fossilized plant remains, which are called macerals. Macerals are differentiated into three major groups: vitrinite, derived from woody plant material (mainly lignin), liptinite, developed from

lipids and waxy plant substances and inertinite, derived from char of prehistoric wood fires. Lignin (Figure 1) is possibly the most important vegetal precursor of vitrinite in coal.

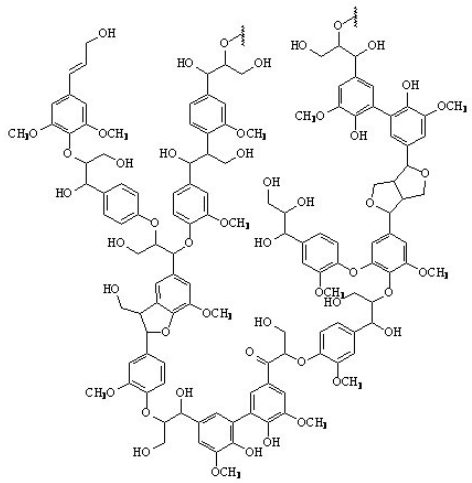


Figure 1: Structure of lignin.

Due to the structure of lignin (Figure 1) the initially monocyclic aromatic units could be condensed with the aliphatic lignin structure to form polycyclic aromatic units of naphthalene or phenanthrene during coalification (Haenel 1992).
The whole coal structure consists of a network of three-dimensionally cross-linked macromolecules, the “immobile” phase, and small molecules within the network, the “mobile” phase. The “mobile” phase is of particular environmental interest because the molecules of this phase are less bound to the macromolecular structure and can be extracted from the matrix. Many different compounds such as phytane, pristane,

PAHs, hopane and other markers could be identified in the “mobile” phase (Haenel 1992).

The distribution of hydrocarbons in coals is dependent on the coal rank. Most coals exhibit 3-5 aromatic rings per structural unit (Stout et al. 2002b). A typical hard coal exhibit 2-6 ring PAH which are linked by methylene bridges with bound aliphatic side chains and phenol functional groups. With increasing rank the aromatic units increase to about 30 fused rings (anthracite).

Achten and Hofmann (2009) compile in their review several investigations of other authors who identified PAHs in hard coals. PAH concentrations of 1 – 2500 mg kg^{-1} were found in coals all over the world. These PAHs include amongst others the sixteen EPA PAHs, perylene, coronene as well as methylnaphthalenes and methylphenanthrenes. The highest concentrations were found in high volatile bituminous coals. Ahrens and Morrisey (2005) found high concentrations of naphthalene and its alkylated derivatives in low hard coal ranks and a relative increase to 4-6 ring PAHs at higher rank coals. Achten and Hofmann (2009) compile these changes in PAH distributions with increasing rank in their paper in Figure 5a-c.

1.3 Toxicity of PAHs

Chapter 1.1 describes the affinity of PAHs to adsorb to particles and accumulate in soils and sediments. Therefore, these soil and sediment bound PAHs may present a potential risk to the aquatic and terrestrial environment.

A couple of PAHs have been identified to exhibit mutagenic and carcinogenic potentials and are widely studied for potential environmental effects (Fang et al. 2004; Hawthorne et al. 2006; Loibner et al. 2003; Neff et al. 2005; Olajire et al. 2005). The carcinogenity of PAHs is for the most part structure dependent (Figure 2).

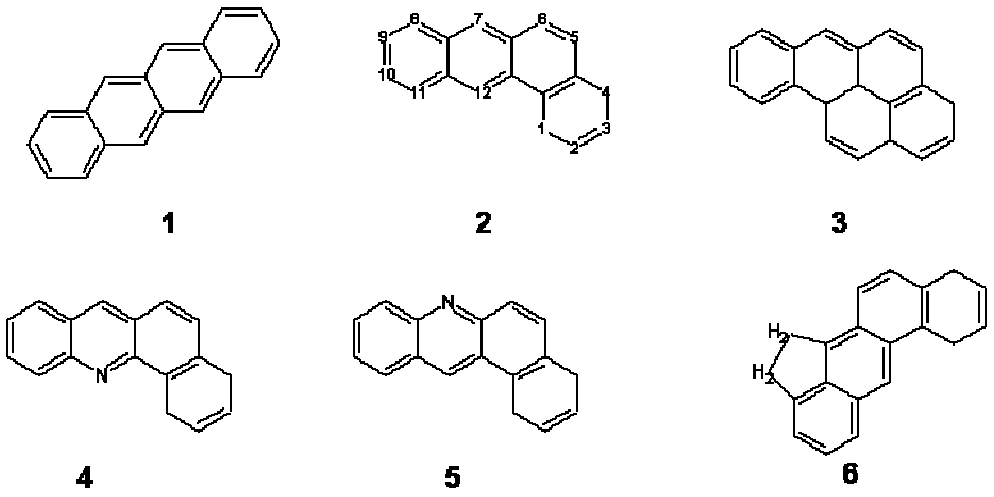


Figure 2: Structure dependent carcinogenity of PAHs with 1) not carcinogenic, 2) low carcinogenic, 3) highly carcinogenic, 4-5) not carcinogenic, 6) extremely carcinogenic (Lowe and Silverman 1984).

Structure one in Figure 2 does not show any carcinogenity, structure two a low carcinogenity and structure three a high carcinogenity. It is found that a C-H replaced by a N (see structure five) tends to loose its carcinogenity, whereas the structure has a higher carcinogenic potential by methylation of position 6, 7 or 12 (see structure six) (Lowe and Silverman 1984). Additionally, the chemical reactivity of a substance is responsible for its toxicity.

The metabolism of PAHs to dihydrodiol epoxides in an organism tends to increase the genotoxic potential of PAHs. The best known PAH to induce cancer is benzo(a)pyrene, and was first identified as a potential carcinogen in coal tar by Cook et al. in 1933 (Cook et al. 1933). In Figure 3 the metabolization of benzo(a)pyrene is shown.

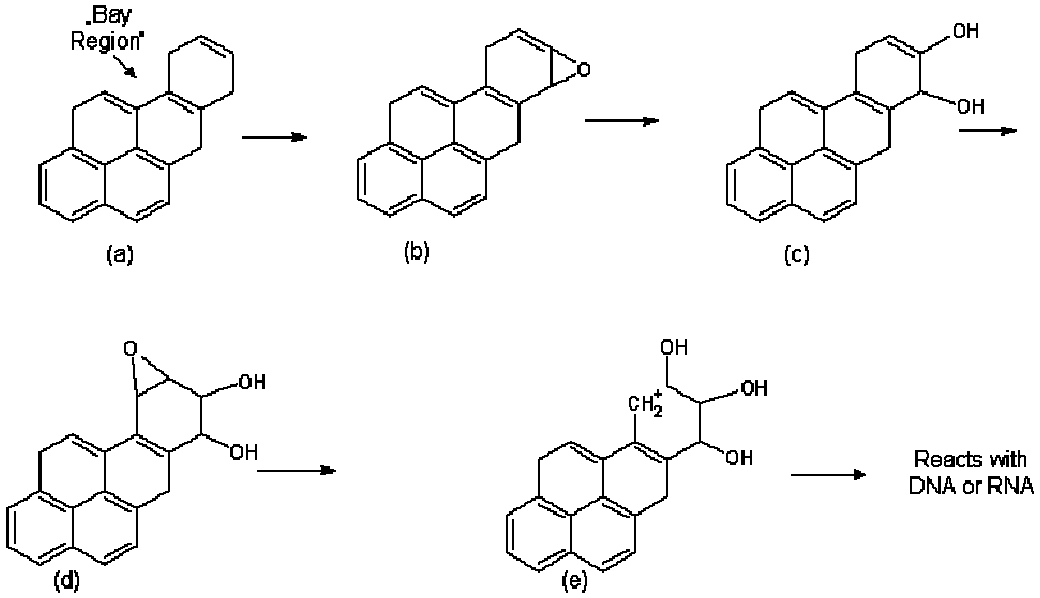


Figure 3: Metabolization of benzo(a)pyrene (Lowe and Silverman 1984).

The transformation product dihydrodiol epoxide (Figure 3d) is called the “ultimative carcinogen”. It binds covalently to DNA (and RNA) and disrupts a number of molecular processes, and can lead to tumour formation (Harvey and Geacintov 1988; Wild and Jones 1995).

Other mutagenic or carcinogenic acting PAHs are mostly four to seven ring compounds, especially benzofluoranthenes, benz(a)anthracene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene and dibenzopyrenes (IARC 1983). Also substituted PAHs exhibiting a bay-region (Figure 3) and a free peri-position situated next to an unsubstituted benzoic ring can produce genotoxic effects, e.g. 5,11-dimethylchrysene, 5-methylchrysene, 1,4- and 4,10-dimethylphenanthrene (Hecht et al. 1979; LaVoie et al. 1982).

The US EPA has identified sixteen PAHs as “priority pollutants” (EPA 1989) except dibenzopyrenes. In addition, there are hundreds of PAH compounds, including alkylated substitutes, which should be considered during risk assessment processes (Barron and Holder 2003; Neff et al. 2005). The European Water Framework Directive only include seven PAHs as “priority pollutants” (i.e. naphthalene, fluoranthene, benz(a)pyrene, benz(b)fluoranthene, benz(k)fluoranthene, indeno(1,2,3-cd)pyrene and benz(ghi)perylene) (Parliament 2000).

However, researchers have identified dibenzopyrenes, especially dibenz(al)pyrene, as the most carcinogenic and mutagenic PAH tested. Dibenz(al)pyrene is reported to be 10 - 100 fold more effective than benz(a)pyrene (Binková and Srám 2004; Cavalieri et al. 1991; Jacob et al. 2004). Therefore, toxic potentials could be underestimated by only using the sixteen EPA PAHs or the seven PAHs from the European Water Framework Directive.

The toxicity potential of individual PAHs is often known but a risk assessment for PAH mixtures in environmental samples is still challenging. Several studies could show synergistic as well as antagonistic interactions between low and high molecular PAHs (Hylland 2006). Other researches demonstrated additive effects of parent PAH mixtures but did not include the alkylated substances. Therefore, the influence of alkylated PAHs could not be evaluated (Hermann 1981). In contrast, Haugen and Peak (1983) reported an inhibition of mutagenic effects between PAHs which resulted in a lower toxicity.

1.4 Overview

In chapter three the extent of PAH contamination in soils collected along the Mosel and Saar River is investigated, and a first insight into the origin of the PAH contamination in this region is obtained. Therefore, 19 PAHs were analyzed, the distribution of PAH concentrations along the Mosel and Saar River were compared, PAH distribution patterns discussed and microscopic analyses used to evaluate the coal mining impact in the investigation area.

In chapter four source identification methods for PAH sources at the Mosel and Saar River are discussed. The distribution patterns of 45 PAHs (including sixteen EPA PAHs and some alkyl PAHs), specific PAH ratios, distribution patterns of n-alkanes and principal component analysis are considered. In addition, the efficiency of the test approaches is assessed. For analyzing a set of 45 PAHs and PAH homologues an analytical method was developed.

In chapter five, there is a discussion if samples collected from point sources and non-point sources can be distinguished by using three forensic methods (i.e. PAH patterns of an extended PAH spectrum, PAH ratios and n-alkanes). In addition, it is assessed if the three methods tested are sufficient for the investigated samples and can be an appropriate tool for distinguishing between point and non-point sources of PAHs in environmental samples.

In chapter six the mutagenicity of soils and sediment along the Mosel River is studied by investigating the mutagenic potential of the soils and sediment with a fluctuation version of the Ames-test.
For that reason soils and sediments were extracted and the PAH fraction was further fractionated into six fractions. These six fractions and the total PAH fraction were tested and evaluated for their mutagenicity.

2 Study Area and sampling sites

Mosel River is located in the German federal state of Rhineland Palatinate. It rises at the Col de Bussang (Vogues Mountains) in France and joins the Rhine River at Koblenz, Germany after 520 km. Approximately 242 km of the river is located in Germany, with several tributaries flowing into the river, including Saar River.

The river flows through the “Rheinische Schiefergebirge” with a lot of sinuosities. The Mosel valley is a narrow valley, with small parts of fluvial deposition areas. The dominant geologic formation is “Hunsrückschiefer” (clay- and siltstone, Devonian). In the southwest the dominant geologic formation is Lacustrine limestone (Trias). The geologic formations are illustrated in the map of the State Office for Geology and Mining Rhineland Palatinate (**Figure 4**).

The Mosel River runs mainly through wine-growing districts and some urban centres with small industries. Since 1964 it is possible to use Mosel River for commercial shipping with big ships. Therefore twenty-eight barrages had to be built, ten in the German part of the Mosel. Now Mosel River is the most used inland water-way in Europe (www.wsa-ko.wsv.de/pressemitteilung-40j.pdf 2004).

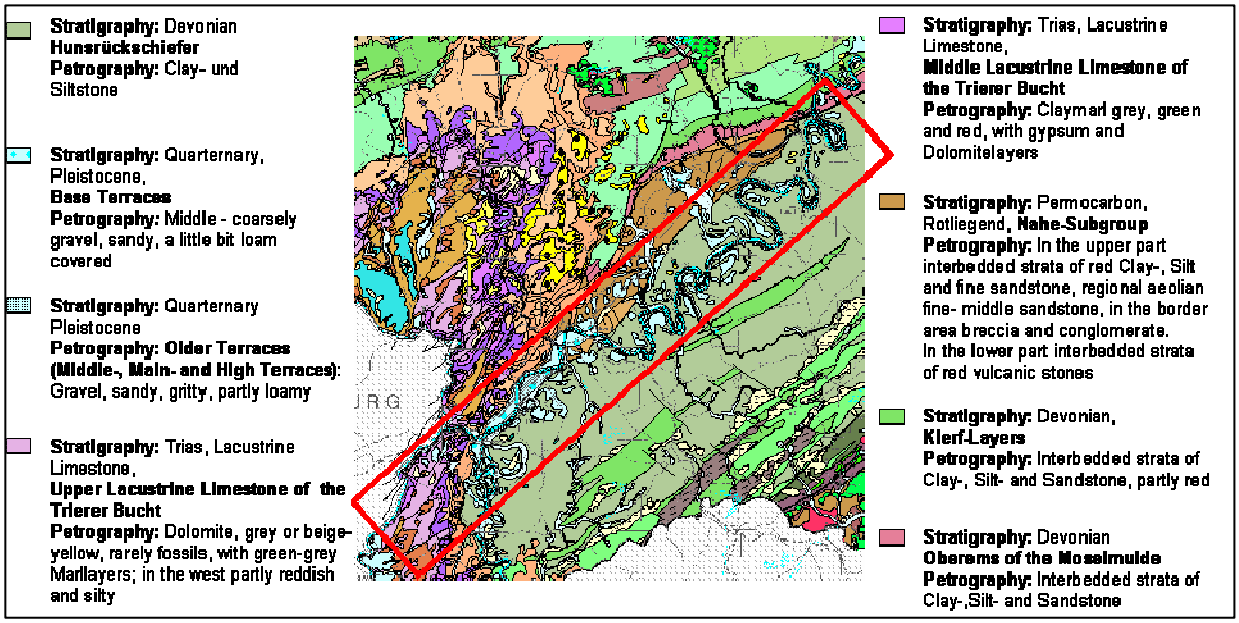


Figure 4: Geological map of the study area (red rectangle) with the relevant caption (www.lgb-rlp.de).

The Mosel River has been regulated as an important waterway since the last 50 ties. The regulation is linked with increasing flood events

Saar River is an important tributary of Mosel River. It flows through Lorraine in France and the Saarland in Germany, where it joins Mosel River. Both regions, Lorraine and Saarland, are well known for coal mining. Coal mining was an important industrial sector in the Saarland. The first coal mine in Saarland can be dated back to the third century B.C. The expansion of coal mining activities since the 16th century resulted in an increase of coal particles transported along Saar River and Mosel River. Floods with water levels rising about 8 to10 m have occurred frequently and spread coal particles onto the floodplains. In addition, human activity along Mosel River has resulted in a number of possible point sources of contamination, including treated wastewater effluents being discharged into the river and surface runoff.

In this study bank soils from twenty-six sampling sites were investigated, three sites along Saar River and twenty-three sites along Mosel River. Altogether forty two individual samples were collected along a 167 km distance of Mosel River and six samples were collected along a 20 km distance of Saar River (Figure 5).

Of the 26 sampling sites, five sites (see Figure 5), were selected for detailed investigation (chapter 4).

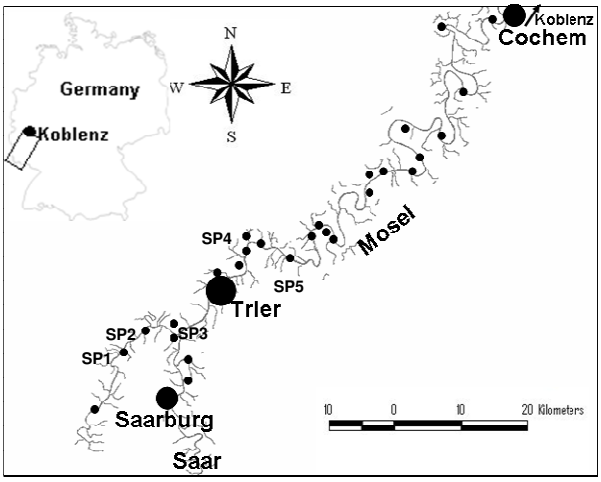


Figure 5: Map of Mosel River in Germany with the location of the 26 sampling sites (small black dots) investigated in chapter 3 and the five sampling points (SP1-SP5) for the detailed investigation described in chapter 4.

Selection criteria were based on the absence of intensive agricultural or recreational use, frequent flooding of the Mosel and Saar Rivers, and the absence of an anthropogenic disturbed soil profile.

All five sampling sites were located in the floodplains. Two sampling points (SP) with a minor coal mining impact were selected and were located upstream of the confluence of the Mosel and Saar Rivers. Sampling point 1 (SP1) was located 10 km upstream of the confluence and sampling point 2 (SP2) was located 3.5 km upstream of the confluence. Three sampling sites impacted by coal mining were also selected, with one directly at the Saar and Mosel Rivers confluence (SP3) and two downstream of the confluence. Sampling point 4 (SP4) was located 18 km downstream of the confluence and sampling point 5 (SP5) was located 42.5 km downstream of the confluence (Figure 5).
The distance of the sampling points to the river was 10 m for SP1, 100 m for SP2, 20 m for SP3, 500 m for SP4, and 50 m for SP5.

3 Coal mining activities and the distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in floodplain soils of the Mosel and Saar River

3.1 Introduction

PAHs are nonpolar organic chemicals with low water solubilities (i.e. high K_{ow} values). Especially high molecular PAHs exhibit a great affinity to adsorb to particles and hence accumulate in soils and sediments (Neff et al. 2005; Youngblood and Blumer 1975). Wild and Jones (1995) estimated that at least 90 % of the environmental PAH burden in Great Britain is stored in soil. This estimation excluded contaminated sites like gasworks sites, petroleum refineries, or wood preservation plants.

Every now and then elevated PAH concentrations were found in alluvial soils along Mosel River. Wieber (2005) investigated one alluvial soil collected in a rural area along the Mosel River. He found PAH concentrations of up to 25 mg kg^{-1} (Σ_{16} EPA PAHs) at depths of 0.3 to 0.9 m and up to 90 mg kg^{-1} at depths of 1.80 to 2.00 m. The PAH content exceeded by far the background levels of the sixteen EPA PAHs in greenland soils in Rhineland Palatinate (2.36 mg kg^{-1} 90 percentile, (LABO 2003)). Rhineland Palatinate has the highest background levels of PAHs in grassland soils of Germany. PAH values reported from other federal states range from 0.43 mg kg^{-1} to 1.3 mg kg^{-1} (90 percentile). Because of the presence of black particles (identified as coal particles in this study) in both contaminated soil layers, Wieber (2005) assumed for the first time that the PAH contaminations may be associated with these particles. However, their origin and the extent of the contamination in the region remained unclear.

The aim of this chapter is (a) to evaluate for the first time the distribution of PAHs in bank and alluvial soils along Mosel and Saar River and (b) to elucidate, if PAH contaminations correlate with soil black (coal) particles or to find out whether the enhanced PAH concentrations in the study area is the result of diffuse or non point source contaminations.

3.2 Material and Methods

Sieve analysis, microscopy and Total Organic carbon (TOC)

Soil samples were gathered from a depth of 0 to 2 m with a stainless steel corer (∅ 8 cm). Each 2 m sample was further separated into two sub-samples (0 to 1 m and 1 to 2 m) and then homogenized. Samples were filled in brown glass bottles and stored at 4° C in the dark. Sieve analysis was performed according to DIN ISO 11277 with the pipette method following Köhn. Different sieve sizes were used: 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and 0.063 mm (Retsch Germany). The samples were dried at 105° C. Each dried sample was investigated with a binocular. Pulverized samples were used for total organic carbon analysis. First, inorganic carbon was removed by adding hydrochloric acid (HCl 16%, p.a. Merck) drop by drop until no further reaction was visible. Afterwards the samples were washed with deionised water until a pH value of 6 was reached. After drying at 100° C, 0.1 g of each sample was analyzed with a CS elemental analyzer (LECO CS 225, St. Joseph, MI).

PAH analysis

Approximately 25 g to 30 g of wet soil were extracted in four cycles with an accelerated solvent extractor (ASE 300, Dionex). Two cycles were performed with acetone at 100° C and 100 mbar and the other two cycles with toluene at 150° C and 100 mbar.

The most common method to extract PAHs from soils is with Soxhlet. However, this method has a relative high solvent consumption and needs relative much time for a few samples. Graham et al. (2006) could show that extraction with ASE is as effective as Soxhlet but with less solvent, less time and more samples. On this account we used ASE in this study.

Perdeuterated internal standards including naphthalene d8 (Nap d8), acenaphtene d10 (Ace d10), phenanthrene d10 (Ph d10), fluoranthene d10 (Flu d10), chrysene d12 (Chr d12) and perylene d12 (Per d12) were added to the extraction solvent.

Depending on their estimated PAH concentration, samples were concentrated with a rotary evaporator after sample extraction. The solvent was exchanged into cyclohexane afterwards. The perdeuterated substances were used for an internal calibration and adapted to the PAH concentrations in the soils.

PAHs were detected using gas chromatography (HP 6890) equipped with a DB-5MS column (0.25 µm film thickness, 0.25 mm x 30 m) and a mass selective detector in the single ion mode (SIM) (HP 5973). Target ions, qualifier and the retention times are given in Table 1.

Source temperature was 300° C. The carrier gas was helium with a flow rate of 0.8 ml min^{-1}. Initial temperature of 65° C was held for 4 min, increased to 270° C and held for 10 min, and then finally increased to 310° C and held for 6.5 min. One µl of each sample was injected in splitless mode. All results were calculated on a dry weight (dw) basis. The limit of quantification for individual substances varied from 0.8 to 3.0 µg kg^{-1}. PAH concentrations were determined by using two standard solutions. One standard solution contained the sixteen EPA PAHs (naphthalene, Nap; acenaphtylene, Any; acenaphtene, Ace; fluorene, Fl; phenanthrene, Ph; anthracene, An; fluoranthene, Flu; pyrene, Pyr; benzo(a)anthracene, BaA; chrysene, Chr; benzo(b)fluoranthene – benzo(k)fluoranthene, BbF-BkF; benzo(a)pyrene, BaP; indeno(1,2,3-cd)pyrene, InP; dibenz(a,h)anthracene, DBA; benzo(g,h,i)perylene, BghiP), as well as 1-methylnaphtalene, 1Mnap, and 2-methylnaphtalene, 2Mnap, which were used to check the presence of the alkyl PAHs. The second solution included the sixteen EPA PAHs and benzo(e)pyrene, BeP and perylene, Per. Perylene was used to check terrestrial PAH inputs. Both solutions were prepared by Dr. Ehrenstorfer GmbH (Augsburg, Germany). All solvents were in the trace analysis quality.

Table 1: Analysed target ions with qualifier and retention times (Ret.-Time).

PAH	Mass	Qualifier 1	Qualifier 2	Ret.-Time [min]
Nap	128	127	102	11.17
2MNap	142	141		12.91
1MNap	142	141		13.14
Any	152	151		15.07
Ace	153	154		15.50
Fl	166	165		16.78
Ph	178	176		19.08
An	178	152		19.20
Flu	202	200		21.99
Pyr	202	101		22.58
BaA	228	114		26.62
Chr	228	226		26.75
BbF-BkF	252	253		31.20
BeP	252	125		32.08
BaP	252	250		32.28
Per	252	253		32.62
InP	276	138		36.77
DBA	278	139		36.96
BghiP	276	138		37.74

3.3 Results and discussion

Soil characteristics

Grain size fractions, TOC, Total Inorganic Carbon (TIC) and the concentrations of the nineteen PAHs detected in the 48 soil samples from Mosel River banks and Saar River banks are listed in Table 2. Sieve analysis and fine grain analysis showed the majority of the soil consisted of a sand and silt mixture. All soil samples had a similar grain size distribution with a clay content that did not exceed 19 %.

The organic carbon content in most samples was around 0.2 % to 3 % (dw), typically found in floodplain sediments (Gocht et al. 2001). A few samples showed elevated TOC values (4 – 13 %) (Table 2).

The samples with high TIC values were from areas upstream of where Saar River enters Mosel River, and found in areas dominated by Lacustrine Limestone.

Coal particles were identified by microscopy analysis with a binocular in Saar River and downstream Mosel River.

Table 2: Soil properties and PAH concentrations of 26 sites (every meter is a 1 m pooled sample, n.d. = not determined).

Sampling Point (in km of the river)	Depth in m	Sand (2 mm – 0.063 mm) in %	Silt (0.063 mm – 0.002 mm) in %	Clay (<0.002 mm) in %	TOC in %	TIC in %	Σ_{16} EPA + 3 PAH in mg kg^{-1}
229	1	63.4	23.5	13.1	0.6	0.5	0.1
229	2	78.5	9.4	12.1	0.2	0.2	0.2
211	1	61.3	30.1	8.7	1.2	3.9	18.1
211	2	56.7	25.9	17.4	0.6	2.6	1.6
204.5	1	65.6	24.1	10.3	0.8	1.8	5.1
204.5	2	71.3	25.0	3.7	0.2	7.2	0.3
0 (Saar)	1	78.8	14.6	6.6	13.3	0.3	72.6
0 (Saar)	2	n.d.	n.d.	n.d.	9.7	1.3	81.5
4 (Saar loop)	1	86.1	9.1	4.9	n.d	n.d	26.3
4 (Saar loop)	2	80.4	10.9	8.7	1.2	0.0	3.2
9 (Saar)	1	89.7	7.2	3.2	5.3	0.3	12.1
9 (Saar)	2	83.0	11.1	5.9	6.0	0.7	20.9
202	1	68.5	22.0	9.5	0.4	0.3	1.6
202	2	67.0	20.5	12.6	0.3	0.1	0.2
188	1	55.0	33.2	11.8	0.5	0.8	0.1
188	2	59.5	29.1	11.5	0.5	0.2	0.0
186	1	74.1	19.4	6.5	2.8	1.8	10.5
186	2	59.3	32.0	8.7	0.3	1.2	0.1
183	1	61.7	27.6	10.7	3.8	4.0	37.4
183	2	48.9	40.7	10.4	0.4	1.3	1.0
180	1	73.7	18.5	7.8	0.1	0.1	0.1
180	2	68.6	17.1	14.3	0.0	0.1	0.0
173	1	73.0	17.2	9.8	6.8	0.8	50.4
173	2	n.d.	n.d.	n.d.	11.9.	1.1	81.0
165.5	1	78.7	19.0	2.3	2.5	0.8	8.8
165.5	2	n.d.	n.d.	n.d.	0.2	0.9	0.1
162.5	1	62.2	29.0	8.8	6.9	0.5	17.3
162.5	2	67.3	25.0	7.7	0.8	0.9	2.7
160.5	1	n.d.	n.d.	n.d.	5.0	0.6	9.0
160.5	2	87.4	10.1	2.6	11.0	0.7	53.7
158.5	1	74.1	20.4	5.5	8.0	0.4	59.5
141	1	75.7	19.2	5.1	5.6	4.6	24.8
138	1	n.d.	n.d	n.d	2.5	2.7	14.4
135.5	1	68.7	24.1	7.2	4.8	1.3	13.1
135.5	2	55.9	35.5	8.6	0.3	0.9	0.2
132	1	67.9	26.0	6.2	0.8	2.5	4.3
132	2	70.3	23.4	6.2	0.1	0.8	0.4
126	1	65.0	24.0	11.0	0.3	0.8	0.4
126	2	69.7	22.4	7.9	0.3	0.6	0.1
118	1	70.6	21.5	7.9	4.0	2.9	42.8
118	2	51.8	36.0	12.2	3.0	2.6	24.5
109	1	53.3	32.4	14.4	1.1	1.8	3.7
109	2	43.8	38.0	18.1	0.1	0.3	0.1
88.5	1	78.4	18.1	3.5	3.2	1.0	21.3
88.5	2	49.8	34.9	15.3	2.2	2.5	6.9
74.5	1	80.1	16.2	3.7	6.6	0.8	27.6
62	1	60.4	32.7	6.9	0.2	0.8	1.3
62	2	51.7	39.4	8.9	0.3	0.3	0.8

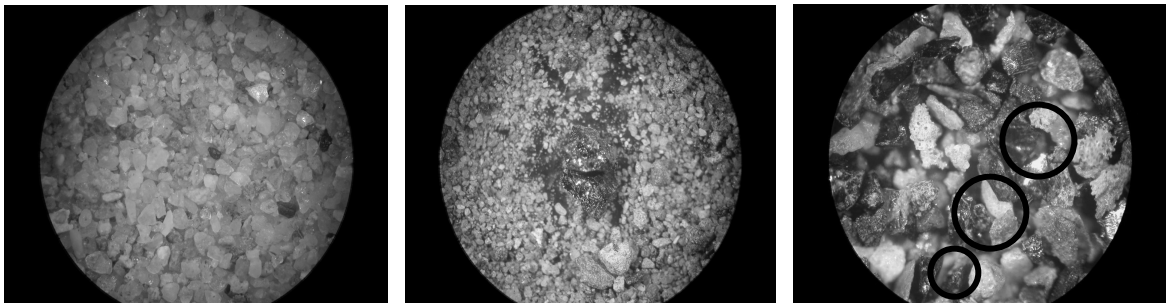


Figure 6: Left picture: sifted sample with a dominance of quartz grains; centre picture: unsifted sample with a big coal particle in the middle, right picture: sifted sample with coal particles (circles).

The picture on the right of Figure 6 shows a typical sifted sample upstream Mosel River with mainly quartz grains. The picture in the middle and on the left of Figure 6 shows black, gleaming particles, identified as coal particles between the quartz grains and other rock fragments in the sifted samples.

PAH distribution along Mosel and Saar River

Most of the bank soils from Saar and Mosel showed elevated PAH concentrations. The concentrations of the sixteen EPA PAHs and the three individual PAHs range from non-detectable to 81 mg kg^{-1} (dw) (Table 2). There was no trend in the distribution of the PAH concentrations along Mosel/Saar River (Table 2). Most of the elevated concentrations were in the first meter of the soil, except at four sample sites. The soils collected from these four sites showed the highest concentrations in the second meter. No point-sources were identified. The PAH concentrations of 11 sample sites exceeded the German guideline value of 20 mg kg^{-1} (LAGA 1998) (Figure 7).

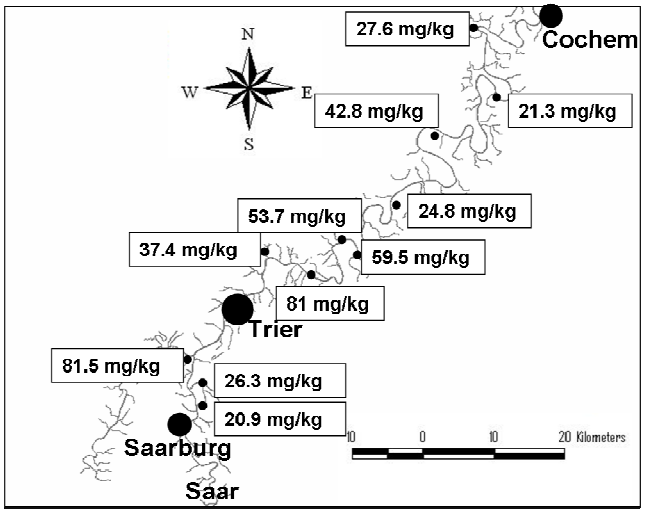


Figure 7: 11 sampling sites with high PAH concentrations.

The PAH distribution pattern of the samples is shown in Figure 8. For the graphs medians with the standard deviations of the PAH concentrations normalized to the total concentration from samples upstream Mosel River (graph A), samples from Saar River (graph B) and samples downstream Mosel River (graph C) were calculated. Due to a higher uncertainty samples with concentrations < 0.2 mg kg^{-1} in the sum of 19 PAHs were not taken into account. The PAH distribution patterns of soil samples at the Saar and downstream Mosel River are similar. They showed high amounts of naphthalene and four to six ring PAHs, whereas fluoranthene and benzo(b)fluoranthene-benzo(k)fluoranthene were the dominating substances.

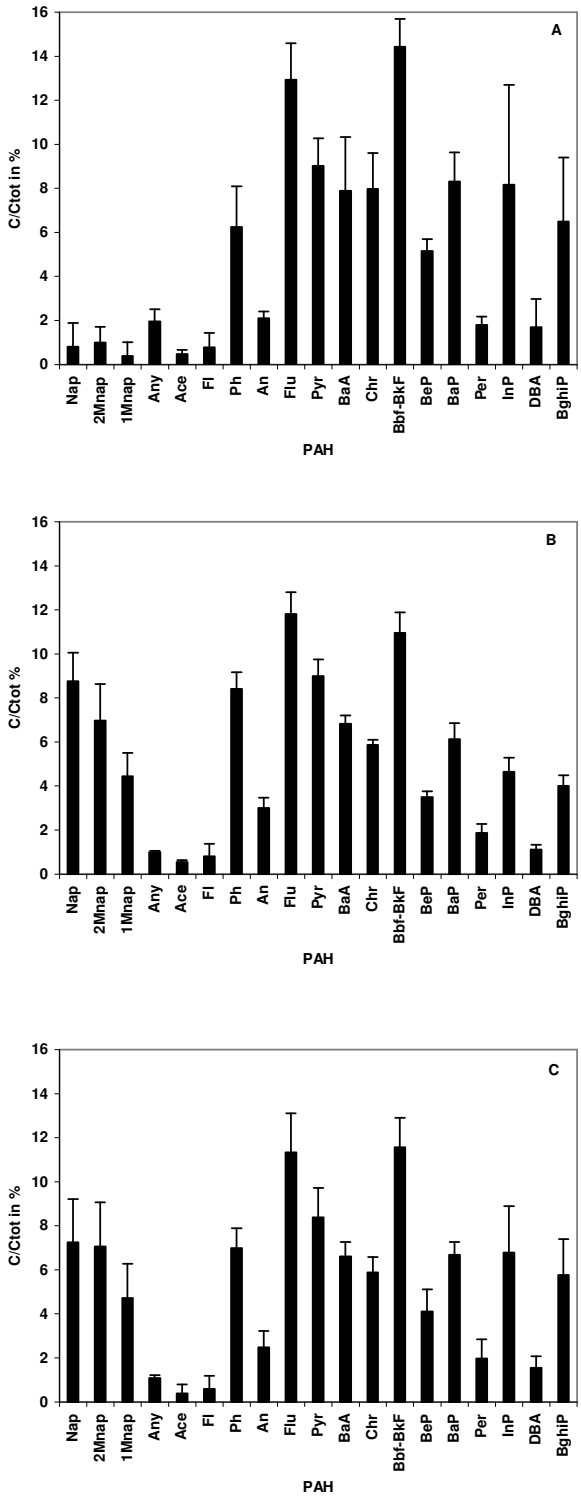


Figure 8: PAH distribution patterns of the medians of the normalized (individual concentration to the total concentration) PAHs and their standard deviations with A: soil samples of Mosel before Saar mouth, B: soil samples of Saar and C: soil samples of Mosel after Saar mouth.

Phenanthrene, pyrene, benzo(a)pyrene, indeno(123-cd)pyrene and benzo(ghi)perylene were elevated too. In contrast, upstream Mosel River lower amounts of naphthalene were determined. The distribution pattern of the higher molecular weight PAHs was similar for all samples.

Heavy weight PAHs are mainly formed by incomplete combustion processes of organic materials (Fernandes et al. 1997). Four to six ring PAHs are primary bound to particles like soot and engine exhaust and substituted PAHs are of minor significance (Sporstöl et al. 1983; Stout et al. 2002a). Typical combustion PAHs (pyrogenic) are fluoranthene, pyrene, indeno(123-cd)pyrene and benzo(ghi)perylene (Fernandes et al. 1997; Page et al. 1996). Lower weight PAHs and substituted PAHs are typical components of petroleum and coals (petrogenic) (Sporstöl et al. 1983; Stout et al. 2002a; Vliex 1994). Vliex (1994) showed a high concentration of naphthalenes and phenanthrenes in Saar coals. This is in accordance with the soil samples from Saar River and downstream Mosel River of this study (Figure 8). In contrast, samples upstream Mosel River exhibited a pyrogenic distribution pattern, i.e. an atmospheric input. The soil samples from Saar River and downstream Mosel River showed a mixed pattern (pyrogenic and petrogenic). The pyrogenic part of the pattern could arise from atmospheric transported coal derived particles from coal industry, traffic emissions and other combustion processes.

PAH concentrations investigated in this study are generally higher compared to other study areas (see Table 3), especially alluvial soils at River Rhine investigated by Gocht et al. (2001).

Table 3: Comparison of PAHs in bank soils of Mosel and Saar River with different soils, sediments and suspended particulate matter from areas worldwide.

Sites	Amount	Range in mg kg^{-1}	Reference
Semirural, agricultural, rural, and forest soils, pasture grassland (all over Great Britain)	49	0.11-54.5	Jones et al. (1989)
Semirural, agricultural soils (southeast England)	9	0.11-1.8	Jones et al. (1989)
Rural, urban and industrial soils (Estonia)	170	0.05-22.2	Trapido et al. (1999)
Rural and urban soils (Hongkong, China)	53	0.03-0.17	Zhang et al. (2006)
Pasture grassland and urban soils (Switzerland)	23	0.05-0.6	Bucheli et al. (2004)
Alluvial soil (Rhine River, Germany)	18	0.02-3.6	Gocht et al. (2001)
Rural and suburban soils (Beijing, China)	47	0.02-3.9	Ma et al. (2005)
Sediments (Gironde estuary, France)	31	0.02-4.9	Budzinski et al. (1997)
Suspended particulate matter (Seine River and estuary, France)	25	1-14	Fernandes et al. (1997)
Suspended particulate matter (Xijiang River, China)	12	0.04-0.67	Deng et al. (2006)
Sediments (Yangtze Estuary, China)	14	0.3-5.5	Liu et al. (2001)
Suspended particulate matter (Elbe River, Germany)	1 year monitoring program	0.1-1.3	ARGE (2001)
Bank soils (Mosel and Saar River, Germany)	42	0.1-81.5	This study

3.4 Conclusions

The investigations of this study showed for the first time large scale PAH contamination in floodplain soils collected from Mosel and Saar River. Twenty six sampling sites were investigated; eleven sampling sites show elevated PAH concentrations up to 81 mg kg^{-1}. In comparison to other regions in the world these concentrations are relatively high.

In addition, for the first time coal particles were identified in most of the soil samples along Mosel and Saar River. Most of the soils with coal particles showed elevated PAH concentrations. Coal can be a source of PAHs, but also a sink due to its high sorption capacity (Barrick et al. 1984; Haenel 1992).

Although the discharge of mine water is decreasing and less coal mining is taking place in the area (IKSMS 2005), contamination from previous mining activities is still evident by the presence of coal particles in the soils. Beside this petrogenic PAHs,

the distribution patterns indicated an additional pyrogenic source downstream Mosel River and at Saar River. Upstream Mosel River only a pyrogenic source can be identified. This pyrogenic input could originate from coal industry (i.e. coal derived particles transported by atmosphere) as well as traffic emissions and combustions processes.

3.5 Recommendation and Perspective

Coal mining activities have a strong impact on the neighbouring regions (Johnson and Bustin 2006; Short et al. 1999; Stout et al. 2002a). It is known that coals exhibit relative high PAH concentrations, especially of low molecular weight PAHs (Chapman et al. 1996; Radke et al. 1990). However, PAHs in coals are hardly bioavailable (Chapman et al. 1996) and hence may have less adverse effects on exposed biota. They can act as sink for other hydrophobic contaminants. Risk assessment of complex environmental samples is difficult due to the identification of the toxic components, the lack of available toxicity data and the scarcity about the knowledge of the behaviour of genotoxic substances in complex mixtures (White 2002). These difficulties are often avoided assuming that the toxicity of a mixture is the sum of the expected effects from each mixture component (EPA 1989). Some substances with high concentrations in this study (i.e. benzo(a)anthracene, benzo(b)fluoranthene-benzo(k)fluoranthene as individual, benzo(a)pyrene, indeno(123-cd)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene) are known to have a sufficient evidence of carcinogenicity in experimental animals (IARC 1983). Hence, high contaminated soil samples in the study area are expected to have a high toxic potential. A detailed study of the sorption, desorption and bioavailability of the PAHs linked to coal particles should be carried out.

4 Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils

4.1 Introduction

Due to increasing environmental awareness contaminated sites are often required to be remediated. Reconstructing past contamination events is getting more and more important and to get information about the contamination source requires specific approaches, commonly referred to as fingerprinting methods. The responsible persons have to be found, and fingerprinting methods or so called environmental forensic methods provide a way of determining who is responsible for the contamination. Especially, due to the toxic relevance of several contaminants (e.g. PAHs) for forensic reasons, an appropriate risk management is crucial to identify their sources.

Fingerprinting is associated with chemical analysis of mixtures (e.g. petroleum products, tars or coals). In a more general sense, fingerprinting techniques or forensic methods include a large diversity of analytical data such as chemical, geological, physical, hydrological, biochemical and biological data (Petrisor 2005). Most articles in this field are related to investigations of forensic aspects of PAHs (Petrisor 2005). Hence, methods to investigate source identification are available, but the heterogeneity of contaminants especially PAHs and the complexity of environmental matrices makes source identification challenging.

However, studies to elucidate PAH sources have focused on sediments, suspended matter and aerosols, with limited research on bank soils (Gocht et al. 2001; Witter et al. 1998). In this study bank soils were in the focus of research. At the study area, elevated sixteen EPA PAH concentrations were reported for bank soils along the Mosel and Saar Rivers (Hofmann et al. 2007; Pies et al. 2007; Yang et al. 2008c; Yang et al. 2008a; Yang et al. 2008b). However, the source of this contamination is uncertain. The objective of this chapter is to identify the source of PAHs in the study area by applying and assessing different source identification methods.

4.2 Material and Methods

4.2.1 Sample collection and preparation

Core soil samples (Ø 8 cm) of two meters were collected, divided into 20 cm sections, and homogenized at each sampling site. Due to the soil characteristics at SP3, only a depth of 140 cm could be reached. A total of 48 subsamples were obtained and stored at 4 °C for two to four days before analysis. Approximately 150 g of each wet sample was filled in aluminum vessels and freeze-dried. Only samples with high concentrations of sixteen EPA PAHs (>20 mg kg^{-1}) were analyzed for the other 45 PAHs. Since the PAH distribution patterns at all depths of a single core were found to be similar, certain depths at each sampling point were selected for detailed investigation of source identification (i.e.120-140 cm for SP1, 0-20 cm for SP2, 80-100 cm for SP3, 40-54 cm for SP4 and 0-20 cm for SP5) (Table 4). All samples were sifted (<2 mm) and pulverized before extraction.

In addition, reference material (original coal samples) from the Saarland region were investigated. The reference material consisted of one high volatile bituminous coal (HVBC), one medium volatile bituminous coal (MVBC) and one anthracite (An). The anthracite and medium volatile bituminous coal samples were taken from the last operating mine in the Saarland region, and high volatile bituminous coal samples were collected from the storage area of a former coal mine in the same region. The general characteristics of the river bank soils at the five sampling sites are summarized in Table 4.

Table 4: Σ_{16} EPA PAH and Σ_{45} PAH concentrations of the five sampling points and three coals against depth including the percentage of EPA PAHs to Σ_{45} PAHs (n.a. = not analyzed). Additionally, samples which were analyzed for C_1-C_4 alkyl-PAHs and n-alkanes are displayed.

Sampling point 1	0-20 cm	20-40cm	40-60 cm	60-80 cm	80-100 cm	100-120 cm	120-140 cm	140-160 cm	160-180 cm	180-200 cm	
Σ_{16} EPA PAHs in mg kg^{-1}	31	64	66	9	13	41	79	56	31	5.7	
Σ_{45} PAHs in mg kg^{-1}	43	86	87	n.a	n.a	56	114	76	n.a	n.a	
% of EPA PAHs to all PAHs	72	74	76			73	69	74			
C_1-C_4 Alkyl PAHs; n-alkanes	analyzed	analyzed	analyzed	n.a	n.a	analyzed	analyzed	analyzed	n.a	n.a	
Sampling point 2	0-20 cm	20-40 cm	40-60 cm	60-80 cm	80-100 cm	100-120 cm	120-140 cm	140-160 cm	160-180 cm	180-200 cm	
Σ_{16} EPA PAHs in mg kg^{-1}	18	13	3	0.5	0.2	2	< 0.2	< 0.2	< 0.2	< 0.2	
Σ_{45} PAHs in mg kg^{-1}	25	18	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	
% of 16 EPA PAHs to all PAHs	72	72									
C_1-C_4 Alkyl PAHs; n-alkanes	analyzed	analyzed	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	
Sampling point 3	0-20 cm	20-40 cm	40-60 cm	60-80 cm	80-100 cm	100-120 cm	120-140 cm	140-160 cm	160-180 cm	180-200 cm	
Σ_{16} EPA PAHs in mg kg^{-1}	30	33	37	72	90	73	128	n.a.	n.a.	n.a.	
Σ_{45} PAHs in mg kg^{-1}	50	52	60	115	140	115	197	n.a.	n.a.	n.a.	
% of 16 EPA PAHs to all PAHs	60	63	62	63	64	63	65				
C_1-C_4 Alkyl PAHs; n-alkanes	analyzed	analyzed	analyzed	analyzed	analyzed	analyzed	analyzed	n.a	n.a	n.a	
Sampling point 4	0-20 cm	20-40 cm	40-54 cm	54-60 cm	60-80 cm	80-100 cm	100-120 cm	120-140 cm	140-160 cm	160-180 cm	180-200 cm
Σ_{16} EPA PAHs in mg kg^{-1}	12	16	53	89	35	10	4	0.6	0.2	< 0.2	< 0.2
Σ_{45} PAHs in mg kg^{-1}	n.a.	n.a.	93	158	53	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
% of 16 EPA PAHs to all PAHs			57	56	66						
C_1-C_4 Alkyl PAHs; n-alkanes	n.a	n.a	analyzed	analyzed	analyzed	n.a	n.a	n.a	n.a	n.a	n.a
Sampling point 5	0-20 cm	20-40 cm	40-60 cm	60-80 cm	80-100 cm	100-120 cm	120-140 cm	140-160 cm	160-180 cm	180-200 cm	
Σ_{16} EPA PAHs in mg kg^{-1}	15	18	18	0.8	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	
Σ_{45} PAHs in mg kg^{-1}	18	22	22	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
% of 16 EPA PAHs to all PAHs	83	82	82								
C_1-C_4 Alkyl PAHs; n-alkanes	analyzed	analyzed	analyzed	n.a	n.a	n.a	n.a	n.a	n.a	n.a	
Coals	HVBC	MVBC	An								
Σ_{16} EPA PAHs in mg kg^{-1}	51	22	13								
Σ_{45} PAHs in mg kg^{-1}	170	69	53								
% of 16 EPA PAHs to all PAHs	30	32	25								
C_1-C_4 Alkyl PAHs; n-alkanes	analyzed	analyzed	analyzed								

4.2.2 PAHs

To analyze the PAHs, 1 to 5 g of freeze-dried and pulverized samples were extracted twice with hexane/acetone (2:1) by Pressurized Liquid Extraction (PLE) using an ASE 200 (160 bar, 120 °C) (Dionex, Idstein, Germany). The two extracts were combined, concentrated to about 5 ml and diluted with hexane according to the PAH concentration of the sample. Internal standard surrogates, including naphthalene d8, acenaphtylene d8, phenanthrene d10, fluoranthene d10, pyrene d10, benzo(a)pyrene d12 and benzo(ghi)perylene d12 (LGC Promochem GmbH Wesel, Germany) were spiked into the concentrated extracts prior to clean up. For the clean up of PAH extracts glass columns were filled with 100 mg of batting and 2 g of copper. Before clean up the columns were conditioned with 10 ml HCl, 25 ml Milli-q water, 20 ml acetone and then hexane (column filled with hexane in the end). Then 2 g neutral alumina oxide (heated by 500° C for 5-6 h and deactivated with 10 g Milli-q water in an overhead shaker for 24 h) was added to the columns. Elution was done with hexane/acetone (98:2). All extracts were reduced to approximately 1 ml by a gentle stream of N_2. The samples were analyzed for PAHs by gas chromatography-mass spectrometry (Agilent GC 6890N, MSD 5975). A list of the target PAHs can be found in Table 5. For GC-MS analyses a volume of 1 µl was injected by an injector temperature of 80° C. The injector was heated with 750° C min^{-1} to 350° C and then cooled down with 10° C min^{-1} to 150° C. The gas chromatography temperature program was maintained at 60° C for 3 min, from 60° C to 150° C in 8° C min^{-1}, from 150° C to 200° C in 3° C min^{-1} and hold for 5 min, from 200° C to 250° C in 5°C min^{-1} and hold for 5 min, from 250° C to 310° C in 10° C min^{-1} and hold for 15 min, from 310° C to 330° C in 10° C min^{-1} and hold for 10 min. A PTV injector was used in the splitless mode. The capillary column was a HP 5-MS (phenyl-methyl-siloxane), 30 m × 0.25 mm ID, 0.25 µm film thickness, and the mass spectrometer was operated under selected ion monitoring mode (SIM). The retention times and mass-to-charge ratios (m/z transitions) of the PAHs are listed in Table 5. The carrier gas was helium with a constant flow rate of 1.3 ml min^{-1}.

In addition, the alkyl homologues C_1-C_4 of naphthalene, fluorene, phenanthrene + anthracene and fluoranthene + pyrene were determined. They were quantified using straight baseline integration of each level of alkylation. For this purpose the known area and concentration of a determined alkyl substance of a soil sample was used to calculate the alkyl homologues (C_2-C_4). That means the concentration and area of 1,2-dimethylnaphthalene was used to quantify C_2 naphthalenes, 2,3,5-trimethyl-naphthalene was used to quantify C_3 and C_4 naphthalenes, 1-methylfluorene was used to quantify C_1-C_4 fluorenes, 2-methylphenanthrene was used to quantify C_1 phenanthrene + anthracene, 3,6-dimethylphenanthrene was used to quantify C_2-C_4 phenanthrene + anthracene and 1-methylpyrene was used to quantify C_1-C_4 fluoranthene + pyrene. The selection criteria for the integration and reporting of each alkylated homologue were based primarily on pattern recognition and the presence of selected confirmation ions.

For calibration 18 calibration points ranging from 2 µg kg^{-1} – 5000 µg kg^{-1} were prepared with a standard mixture from LGC Promochem GmbH Wesel, Germany containing 43 PAHs. 1,7-dimethylphenanthrene and 3-methylphenanthrene were prepared separately.

The calibration showed two different gradient zones, hence two quadratic fittings ($y = ax^2+bx+c$) from 2 µg kg^{-1} – 600 µg kg^{-1} and 600 µg kg^{-1} – 5000 µg kg^{-1} were used. The correlation coefficient always exceeded 0.99. The noise signal for each compound was determined as the mean value of the measured peak heights in blank samples (hydro material, International Sorbent Technology Ltd, UK, Part. No. 9800-5000) which underwent the same procedure as soil samples. To determine the limit of quantification (LOQ), the signal to noise ratio of each compound was multiplied by nine. Each PLE series (13 samples) included one of the following certified reference materials: SRM 1941b from NIST (organics in marine sediments), EDF 5184 from Ceriliant (organics in soil) and EBS (an internal laboratory reference material of a harbor sediment). Recoveries of these reference materials and reference solutions are given in Table 6. At least two samples of each core were analyzed in duplicate. To confirm the reliability of the GC-MS runs, a low-level analytical standard solution (100 ppm) of PAHs was analyzed after every tenth sample (Table 6).

Table 5: Analyzed PAHs (EPA-PAH with check mark), retention times, masses and qualifier of the analyzed compounds.

Compound	Retention Time (min)	Mass	Qualifier 1	Qualifier 2
Naphthalene (Nap) ✓	9.921	128	127	129
2-Methylnaphthalene (2-MNap)	11.923	142	141	143
1-Methylnaphthalene (1-MNap)	12.222	142	141	143
2,3-Dimethylnaphthalene (2,3-DNap)	14.354	156	141	155
1,2-Dimethylnaphthalene (1,2-DNap)	14.613	156	141	155
2,3,5-Trimethylnaphthalene (2,3,5-TNap)	16.581	170	155	165
Acenaphthylene (Any) ✓	14.514	152	153	151
Acenaphthane (Ace) ✓	15.125	154	153	152
Fluorene (Fl) ✓	16.946	166	165	167
1-Methylfluorene (1-MNap)	19.577	180	165	178
Dibenzothiophene (Dibenzo)	20.654	184	185	189
Phenanthrene (Phe) ✓	21.301	178	179	176
Anthracene (Ant) ✓	21.537	178	179	170
1-Methylanthracene+ 9-Methylphenanthrene) (1-MAnt + 9-MPhe)	24.884	192	191	189
2-Methylphenanthrene (2-MPhe)	24.345	192	191	189
3-Methylphenanthrene (3-MPhe)	24.196	192	191	189
1-Methylphenanthrene (1-MPhe)	24.965	192	191	189
2-Methylanthracene (2-MAnt)	24.572	192	191	189
9-Methylanthracene (9-MAnt)	25.867	192	191	189
3,6-Dimethylphenanthrene (3,6-DPhe)	27.198	206	189	191
1,7-Dimethylphenanthrene (1,7-DPhe)	28.189	206	191	189
Fluoranthene (Flu) ✓	28.511	202	203	200
Pyrene (Py) ✓	29.865	202	200	203
1-Methylpyrene (1-MPy)	34.431	216	215	217
Benzo(a)fluorene (B(a)fl)	32.703	216	215	217
Benzo(b)naphtho(2,1-d)thiophene (B(b)naph(2,1-d)th)	38.422	234	235	232

Compound	Retention Time (min)	Mass	Qualifier 1	Qualifier 2
Cyclopenta(cd)pyrene (Cpenta(cd)Py)	40.151	226	226	223
Benzo(a)anthracene (B(a)Ant) ✓	40.431	228	229	226
Chrysene + Triphenylene (Chr + Tri) ✓	40.704	228	229	227
1-Methylchrysene (1-MChr)	44.283	242	241	239
2-Methylchrysene (2-MChr)	43.715	242	241	239
3-Methylchrysene (3-MChr)	43.557	242	241	239
5-Methylchrysene (5-MChr)	43.918	242	241	209
Benzo(b)fluoranthene (B(b)Flu) ✓	47.096	242	253	250
Benzo(k)fluoranthene (B(k)Flu) ✓	47.236	252	253	250
Benzo(a)fluoranthene (B(a)Flu)	47.693	252	253	250
Benzo(e)pyrene (B(e)Py)	48.652	252	250	253
Benzo(a)pyrene (B(a)Py) ✓	48.945	252	250	253
Perylene (Per)	49.539	252	250	253
Indeno(1,2,3-cd)pyrene (Indeno) ✓	54.955	276	277	281
Dibenzo(ah)anthracene (D(ah)Ant) ✓	55.169	278	280	276
Benzo(ghi)perylene (B(ghi)Per) ✓	55.697	276	274	281
Anthanthrene (Anth)	56.054	276	280	276
C_2-alkylnaphthalenes	11.5-15.5	156	-	-
C_3-alkylnphthalenes	12.5-16.5	170	-	-
C_4-alkylnaphthalenes	13-16.5	184	-	-
C_1-alkylfluorenes	15-16.5	180	-	-
C_2-alkylfluorenes	16-18	194	-	-
C_3-alkylfluorenes	15-25	208	-	-
C_4-alkylfluorenes	15-25	222	-	-
C_1-alkylpenanthrenes + anthracenes	17-18.8	192	-	-
C_2-alkylphenanthrenes + anthracenes	17.8-19.6	206	-	-
C_3-alkylphenanthrenes + anthracenes	18.8-24	220	-	-
C_4-alkylphenanthrenes + anthracenes	19-26	234	-	-
C_1-alkylfluoranthenes + pyrenes	19.8-23.2	216	-	-
C_2-alkylfluoranthenes + pyrenes	20-25	230	-	-
C_3-alkylfluoranthenes + pyrenes	21-26	244	-	-
C_4-alkylfluoranthenes + pyrenes	21.5-28	258	-	-

Table 6: Limit of Quantification (LOQ in µg kg^{-1}, related to 10 g weighted samples), recoveries (in %) and standard deviations (STD) of 45 PAHs in reference solutions and materials.

		100 ppb (n=33)a	5184 (n=6)b	1491a (n=7)c	1941b (n=12)d	NEe (n=10)	EBS (n=15)f
	LOQ	Recovery ± STD	Recovery ± STD	Recovery ± STD	Recovery ± STD	Recovery ± STD	Recovery ± STD
Nap	2-4	109 ± 6	140 ± 21	-	98 ± 5	97 ± 5	148 ± 39
2Mnap	1 4	99 ± 18	-	145 ± 37	111 ± 8	-	-
1MNap	1-2	105 ± 17	-	129 ± 30	106 ± 5	-	-
2,3DNap	0.2-1	103 ± 15	-	-	-	-	-
1,2DNap	0.04-1	102 ± 16	-	98 ± 21	-	-	-
2,3,5DNap	0.2-0.6	107 ± 20	-	-	82 ± 11	-	-
Any	0.02-0.2	101 ± 11	121 ± 10	-	119 ± 26	86 ± 8	-
Ace	0.2-2	106 ± 13	92 ± 21	-	116 ± 21	96 ± 6	312 ± 59
Fl	0.2-2	108 ± 13	68 ± 5	-	77 ± 16	95 ± 10	69 ± 15
1MFl	0.1-0.3	112 ± 15	-	-	-	-	-
Dibenzo	0.06-0.2	106 ± 8	-	-	-	-	-
Phe	0.8-2	110 ± 6	86 ± 4	-	99 ± 4	97 ± 4	83 ± 12
Ant	0.2-0.4	110 ± 21	92 ± 12	-	93 ± 9	77 ± 17	111 ± 8
1MPhe + 9MPhe	0.1-0.6	127 ± 40	-	108 ± 23	78 ± 13	-	-
2MPhe	0.08-0.4	111 ± 23	-	119 ± 28	91 ± 12	-	-
3MPhe	0.05-0.2	-	-	154 ± 57	-	-	-
1MAnt	0.1-0.7	129 ± 24	-	-	-	-	-
2MAnt	0.05-0.4	86 ± 63	-	146 ± 53	174 ± 56	-	-
9MAnt	0.04-0.4	130 ± 21	-	-	-	-	-
3,6DPhe	0.04-0.2	126 ± 16	-	-	-	-	-
1,7DPhe	0.08-1.6	-	-	141 ± 32	-	-	-
Flu	0.05-0.6	114 ± 14	87 ± 6	-	87 ± 10	104 ± 11	92 ± 19
Py	0.2-0.8	111 ± 13	88 ± 9	-	86 ± 10	93 ± 6	80 ± 16
1MPy	0.08-0.6	113 ± 40	-	151 ± 42	111 ± 22	-	-
B(a)fl	0.08-0.4	137 ± 36	-	-	-	-	-
B(b)naph(2,1-d)th	0.05-0.4	130 ± 35	-	-	-	106 ± 15	-
Cpenta(cd)Py	0.08-0.4	141* ± 94	-	-	-	176 ± 70	-

Cont. Table 6							
		100 ppb (n=33)a	5184 (n=6)b	1491a (n=7)c	1941b (n=12)d	NEe (n=10)	EBS (n=15)f
	LOQ	Recovery ± STD	Recovery ± STD	Recovery ± STD	Recovery ± STD	Recovery ± STD	Recovery ± STD
B(a)Ant	0.05-0.2	119 ± 57	105 ± 44	-	106 ± 20	85 ± 39	126 ± 38
Chr + Tri	0.16-0.6	120 ± 57	67 ± 60	-	132 ± 25	149 ± 52	105 ± 26
1MChr	0.08-0.4	151* ± 58	-	-	-	-	-
2MChr	0.08-0.4	157* ± 68	-	-	-	-	-
3MChr	0.3-1.2	-	-	93 ± 39	-	-	-
5MChr	0.08-1.2	140* ± 45	-	-	-	-	-
B(b)Flu	0.2-1.2	119 ± 14	113 ± 3	-	106 ± 5	91 ± 13	67 ± 24
B(k)Flu	0.3-1.6	101 ± 17	82 ± 14	-	130 ± 27	100 ± 29	105 ± 32
B(a)Flu	0.3-1.6	115 ±12	-	-	115 ± 18	-	-
B(e)Py	0.2-1	110 ± 12	96 ± 10	-	115 ± 9	88 ± 11	89 ± 14
B(a)Py	0.3-0.8	120 ± 29	117 ± 22	-	72 ± 21	115 ± 21	88 ± 24
Per	0.4-1.8	-	102 ± 11	-	103 ± 19	104 ± 11	-
Indeno	0.2-0.6	117 ± 26	75 ± 9	-	92 ± 5	86 ± 18	78 ± 17
D(ah)Ant	0.3-1.2	102 ± 57	89 ± 22	-	117 ± 38	170 ± 97	50 ± 34
B(ghi)Per	0.2-1	123 ± 15	93 ± 7	-	85 ± 11	99 ± 17	86 ± 5
Anth	0.2-0.4	118 ± 24	-	-	-	100 ± 9	-

[a] 100 ppb standard solution with 41 substances of 45 to control GC-MS run; [b] Reference soil; [c] Reference solution with alkylated PAHs; [d] Reference sediment; [e] internal reference harbor sediment, [f] Reference solution (b,d,e were used in the whole preparation procedure, c,f were used from the clean up on); * no total separation of compounds possible; - are not reported for the respective reference solution/-material.

4.2.3 n-Alkanes

A slightly modified DIN ISO 16703 (DIN 2002) method was used for the determination of n-alkanes. The samples were freeze-dried and pulverized with a ball mill from Fritsch (Idar-Oberstein, Germany). The pulverized samples were extracted via PLE (160 bar, 120 °C) by a 9:5:1 isohexane/acetone/heptane solution spiked with a standard containing n-decane (C10) (30 µl L^{-1}), n-undecane (C11) (30 µl L^{-1}) and n-tetracontane (C40) (30 mg L^{-1}). After the extract was concentrated to 2 ml the sample

was cleaned by using a 2.4 g Florisil filled column. The extracts were analyzed by gas chromatography coupled with a flame ionization detector (GC-FID, Chrompack 9002). Details of the measurements and data analysis are described in DIN ISO 16703. In this study the CPI developed by Radke et al. (1980) was used for calculations.

4.2.4 Principal Component Analysis

Principal component analysis (PCA) was done with the program STATISTICA© 7.1. In this study, values below LOQ were not considered and the PCA was performed with normalized data. Individual PAH concentrations were divided by the total concentrations of all 45 PAHs, and then multiplied by 100 (Johnson et al. 2002). Hence, a matrix of forty five individual PAH percentages in twenty four samples were obtained. This procedure was found to provide plausible results although it has to be taken into account that it also might lead to incorrect correlations (Pawlowsky-Glahn and Egozcue 2006).

4.2.5 Coal Petrography

Coal petrographic analyses were performed by DSK Ruhranalytik in Herne, Germany. Two soil samples (subsample of SP3 and SP4) containing coal particles were incorporated into synthetic resin and polished. The samples were analyzed under UV and violet-light illumination (fluorescence mode), and white-light using a polarization direct light microscope (Zeiss, magnification 300×).

4.3 Results and discussion

4.3.1 Soil characteristics

All soil samples consisted of a sand and silt mixture. Table 4 lists the concentrations of the Σ_{16} EPA PAHs and the Σ_{45} PAHs for all soil samples and investigated coals. They ranged from <0.2 – 128 mg kg^{-1} for the Σ_{16} EPA PAHs and from 18 – 197 mg kg^{-1} for the Σ_{45} PAHs. The PAH distribution patterns of the sixteen EPA PAHs were the same with depth at each individual site.

Coal petrographic analyses identified particles of hard coal and coal derived materials (e.g. coke and fly ash) in the soils of SP3 and SP4 (Figure 9).
Detailed organic petrographic analysis of the light fractions (ρ <2 g cm^{-3}) of SP1 revealed some coal particles (mostly sub-bituminous coal), and a large abundance of coal derived particles (e.g. coke carbon forms, char, soot and fly ash). In contrast, more coal particles than coal-derived particles were identified in the light fractions at SP3 and SP5 (Yang et al. 2008a).

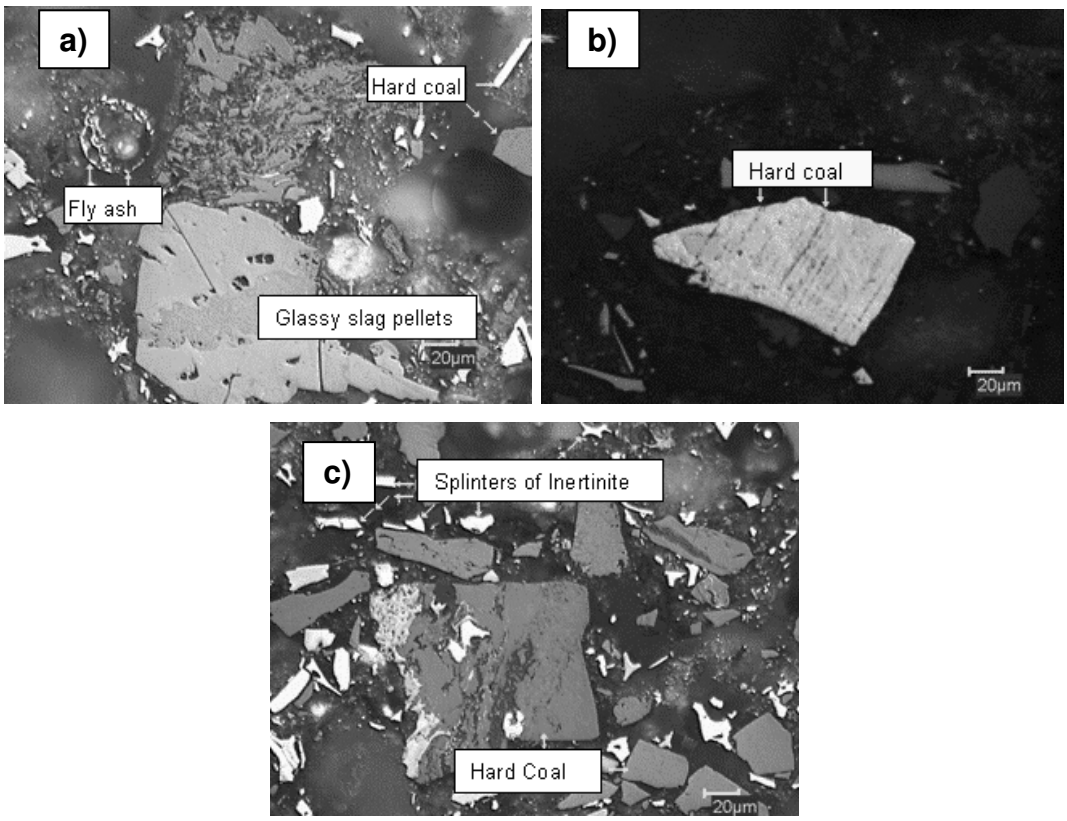
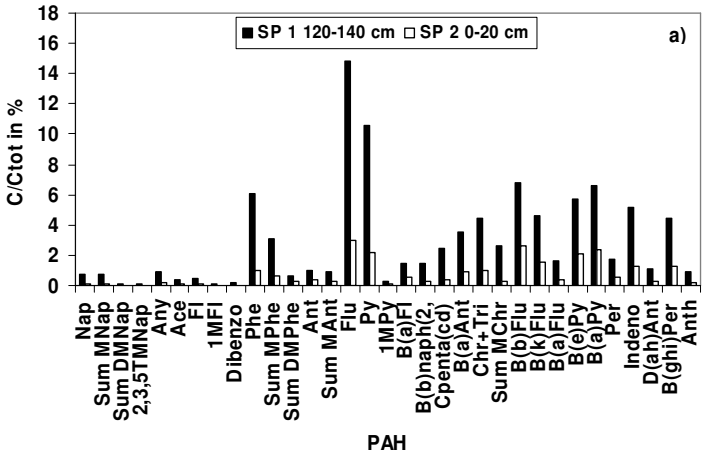


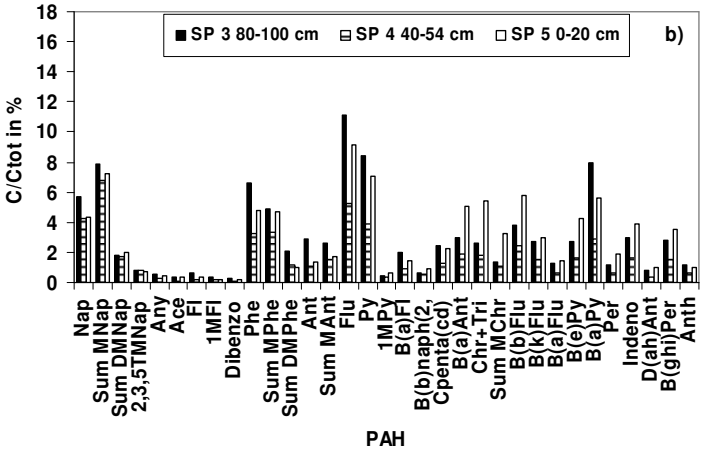
Figure 9: Petrographic identification of coal and coal derived particles in a) and b) SP3 (80-100 cm) and c) SP4 (40-54 cm).

4.3.2 PAH distribution patterns

The PAH distribution patterns of the studied samples are shown in Figure 10. At SP1 and SP2 a low abundance of two to three ring PAHs and alkylated PAHs were found, but PAHs with four to six rings were found to be dominant (Figure 10a). In contrast, distribution patterns of the samples collected from SP3 to SP5 showed a high

abundance of two ring PAHs (naphthalenes and methylnaphthalenes), followed by fluoranthene, pyrene, phenanthrene and five to six ring PAHs (Figure 10b).





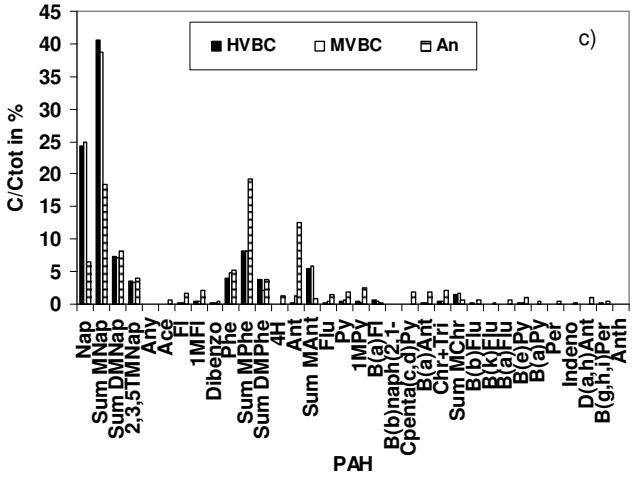


Figure 10: PAH distribution patterns of the five sampling points (SP1 to SP5) and three coals (HVBC = high volatile bituminous coal, MVBC = medium volatile bituminous coal and An = anthracite).

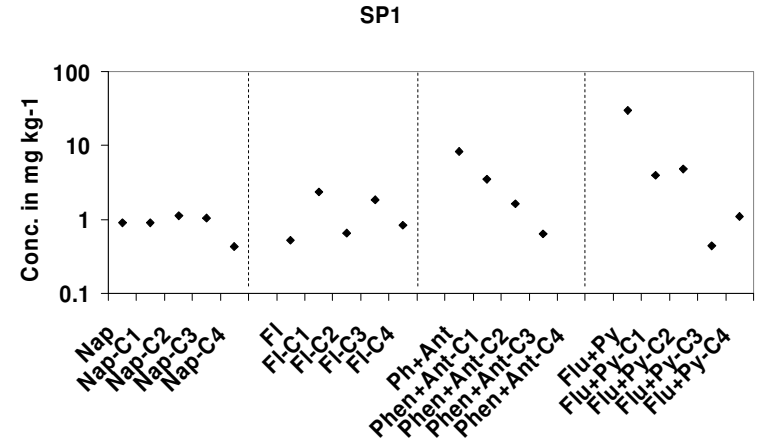
The major difference in the PAH distribution pattern between the sampling locations located upstream and downstream of the confluence was the presence of two ring PAHs, methylnaphthalenes and methylphenanthrenes, at the downstream sampling locations. High naphthalene concentrations have been found in coals (Amijaya 2005; Stout et al. 2002a) and Saar coals (Vliex, 1994). A direct analysis of the Saar coals (i.e. high volatile bituminous coal, middle volatile bituminous coal and anthracite) confirmed the presence of naphthalene (Figure 10c). Therefore, the major difference in PAH distribution patterns between the soil samples of SP1-SP2 and SP3-SP5 is probably due to the presence of coal particles. Thus, the PAH distribution pattern of SP1 and SP2 with the low abundance of two to three ring PAHs and alkylated PAHs, and the dominance of four to six ring non-alkylated PAHs indicate a pyrogenic input (Benlahcen et al. 1997; Boehm et al. 1997; Laflamme and Hites 1978). In contrast, the high contents of four to six ring PAHs plus the high content of two ring and alkylated PAHs in SP3-SP5 suggest a mixture of petrogenic and pyrogenic inputs.

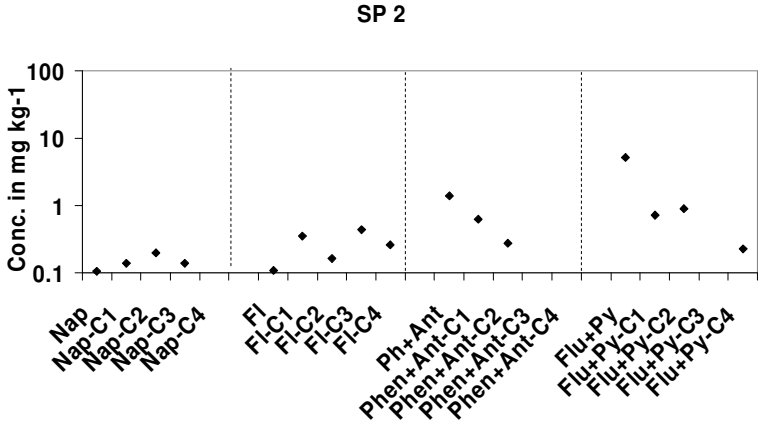
The samples collected from SP1 and SP2 showed a pyrogenic signal with the alkyl homologues, i.e. decreasing concentrations in the C_1-C_4 homologues (Murphy and Morrison 2002) significantly outweighing the petrogenic signal, i.e. bell-shaped distribution in the C_1-C_4 homologues (Murphy and Morrison 2002). In addition, a bell-

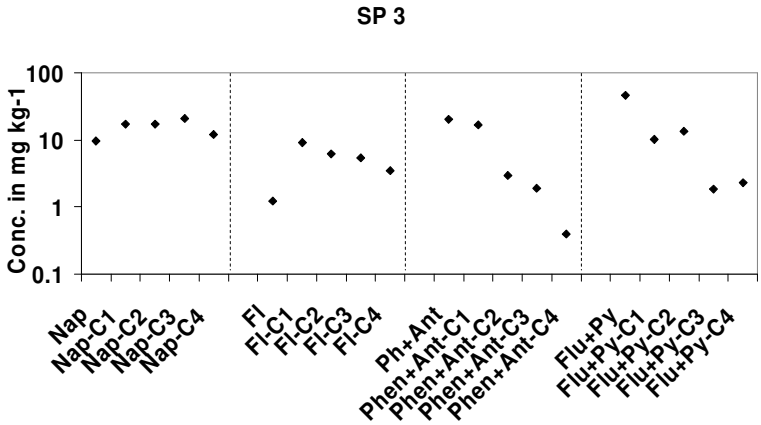
shaped distribution occurred in the low concentrated naphthalenes and fluorenes (Figure 11). All samples of SP3-SP5 showed bell-shaped distributions in the high concentrated naphthalenes and fluorenes, and mainly skewed distributions in the phenanthrenes + anthracenes and fluoranthenes + pyrenes (i.e. mixed sources, Figure 11). The bell-shaped distribution and the high concentrations of substituted naphthalenes and fluorenes strongly suggest that coal particles from mining activities in the Saarland are the most likely source of the PAHs.

The alkyl homologue distribution is sensitive to weathering effects and can give an indication about the proportion of pyrogenic and petrogenic inputs as long as homologue series are considered to be unaffected by weathering. For example, degradation can change a pyrogenic profile into a petrogenic profile with an alkyl homologue distribution of $C_0<C_1<C_2<C_3$, which is true especially for two ring PAHs (Murphy and Morrison 2002). Therefore, the slight bell-shaped distributions in naphthalenes of SP1-SP2 could reflect weathering, due to the low abundance of coal particles in these soils. Alkyl PAH distribution patterns of naphthalene in the reference materials and their similarities to those in samples collected from SP3-SP5 indicate the PAHs are from coal (Figure 10 and Figure 11). As described in chapter 0 low molecular PAHs are the most likely PAHs which can be extracted from hard coals. These low molecular PAHs, detected in SP3-SP5 originate from coal because usually due to their high volatility two and three ring PAHs are found in minor concentrations in the environment. It could be assumed that the analyzed high molecular PAHs were adsorbed to coal particles and other organic materials. Sorption experiments were done and described in more detail by Yang (2007).

Nevertheless, it could not be ruled out, that petroleum inputs due to shipping activities on the rivers as well as refineries upstream the Mosel river (France) also contribute to the PAH contamination in the bank soils.


SP1
Conc. in mg kg-1
100
10
1
0.1
Nap
Nap-C1
Nap-C2
Nap-C3
Nap-C4
Fl
Fl-C1
Fl-C2
Fl-C3
Fl-C4
Ph+Ant
Phen+Ant-C1
Phen+Ant-C2
Phen+Ant-C3
Phen+Ant-C4
Flu+Py
Flu+Py-C1
Flu+Py-C2
Flu+Py-C3
Flu+Py-C4


SP 2
Conc. in mg kg-1
100
10
1
0.1
Nap
Nap-C1
Nap-C2
Nap-C3
Nap-C4
Fl
Fl-C1
Fl-C2
Fl-C3
Fl-C4
Ph+Ant
Phen+Ant-C1
Phen+Ant-C2
Phen+Ant-C3
Phen+Ant-C4
Flu+Py
Flu+Py-C1
Flu+Py-C2
Flu+Py-C3
Flu+Py-C4


SP 3
Conc. in mg kg-1
100
10
1
0.1
Nap
Nap-C1
Nap-C2
Nap-C3
Nap-C4
Fl
Fl-C1
Fl-C2
Fl-C3
Fl-C4
Ph+Ant
Phen+Ant-C1
Phen+Ant-C2
Phen+Ant-C3
Phen+Ant-C4
Flu+Py
Flu+Py-C1
Flu+Py-C2
Flu+Py-C3
Flu+Py-C4

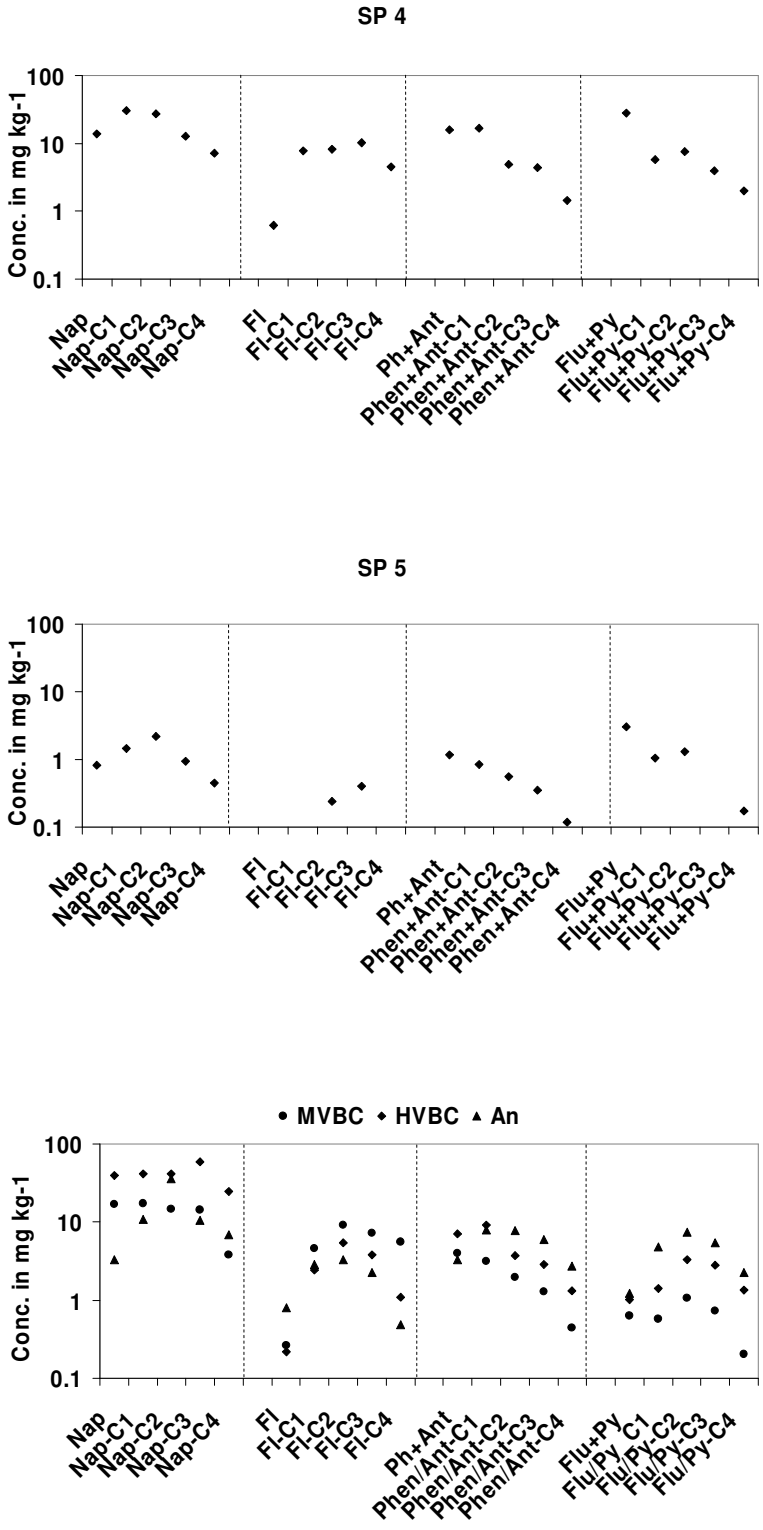


Figure 11: PAH alkyl homologue profiles of selected soils of SP1 (120 - 140 cm), SP2 (0 - 20 cm), SP3 (120 - 140 cm), SP4 (54 - 60 cm) and SP5 (0 - 20 cm) and of three coals (HVBC, MVBC and An).

4.3.3 PAH ratios

As shown in the cross plot of Figure 12a, all investigated soil samples showed a pyrogenic origin. Frequently used ratios to differentiate between combustion and petroleum sources are PAHs of molecular mass 178 (phenanthrene, anthracene) and 202 (fluoranthene, pyrene) (Budzinski et al. 1997; Gschwend and Hites 1981; Sicre et al. 1987). A ratio of anthracene/(anthracene + phenanthrene) <0.1 usually accounts for petroleum, while a ratio >0.1 accounts for combustion (Budzinski et al. 1997; Yunker et al. 2002). The ratio of fluoranthene/(fluoranthene + pyrene) of 0.5 is defined as the boundary between petroleum and combustion (Budzinski et al. 1997; Yunker et al. 2002).

However, the petroleum boundary seems to be closer to 0.4 than 0.5, thus ratios between 0.4 and 0.5 are more characteristic of liquid fossil fuels and >0.5 are characteristic of grass, wood or coal combustion (Yunker et al. 2002).

In this study, C_1 phenanthrenes and anthracenes ratios show the petrogenic influence of samples collected from SP3-SP5 (more coal impacted soils) (Figure 12b). They are in the petroleum or combustion section and near the boundary between the combustion and petroleum regions. If the methylphenanthrene/phenanthrene ratio and the fluoranthene+pyrene/(fluoranthene+pyrene+(C_{2-4} phenanthrene+anthracene)) ratio are included the petrogenic origin is more evident for these samples (Figure 12c).

Also, coals may exhibit values, which actually fit into both sources (Figure 12a-c). In contrast, the samples collected from SP1-SP2 show a pyrogenic influence based on the methylphenanthrene/phenanthrene ratio and the fluoranthene+pyrene/(fluoranthene+pyrene+(C_{2-4} phenanthrene+anthracene)) ratio (Figure 12c). According to the fluoranthene+pyrene/(fluoranthene+pyrene+(C_{2-4} phenanthrene+anthracene)) ratio, SP1 and SP2 exhibit a pyrogenic PAH assemblage, and SP3 to SP5 a mixed PAH assemblage (Neff et al. 2005) (Figure 12c).

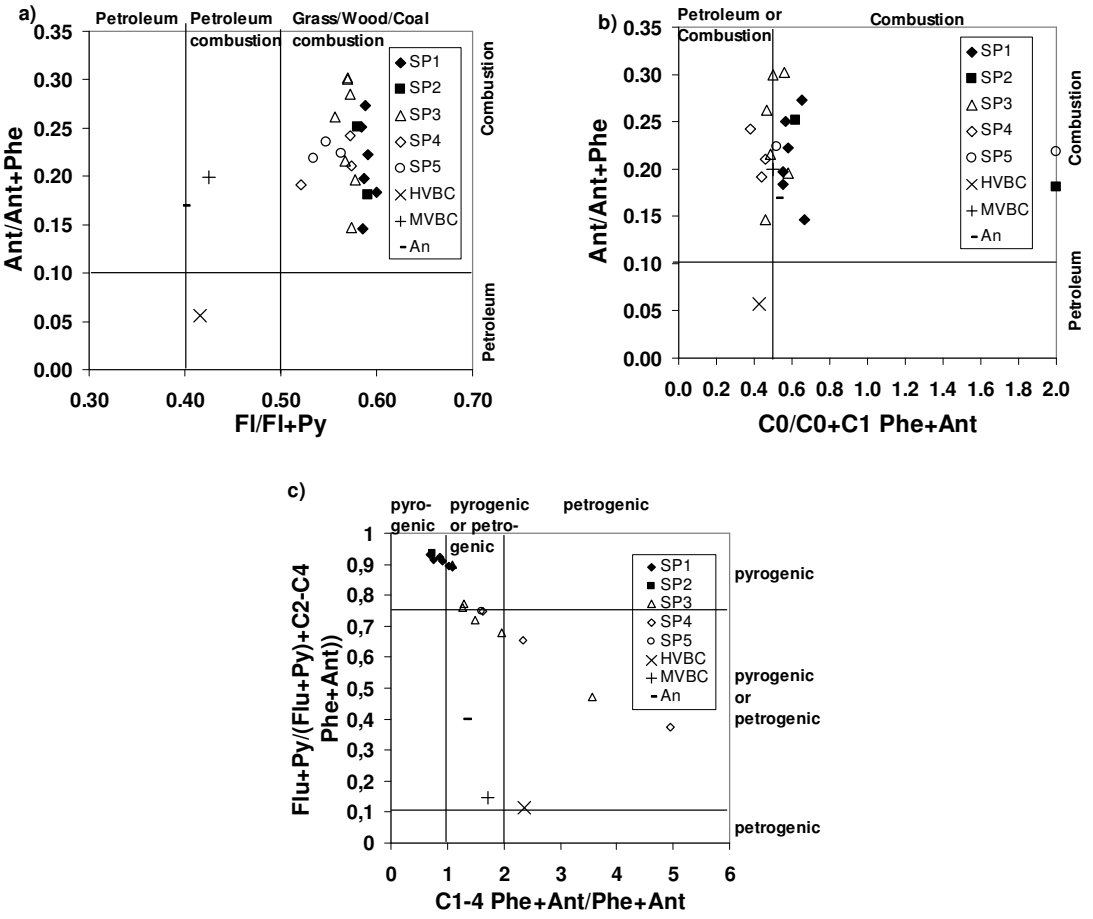
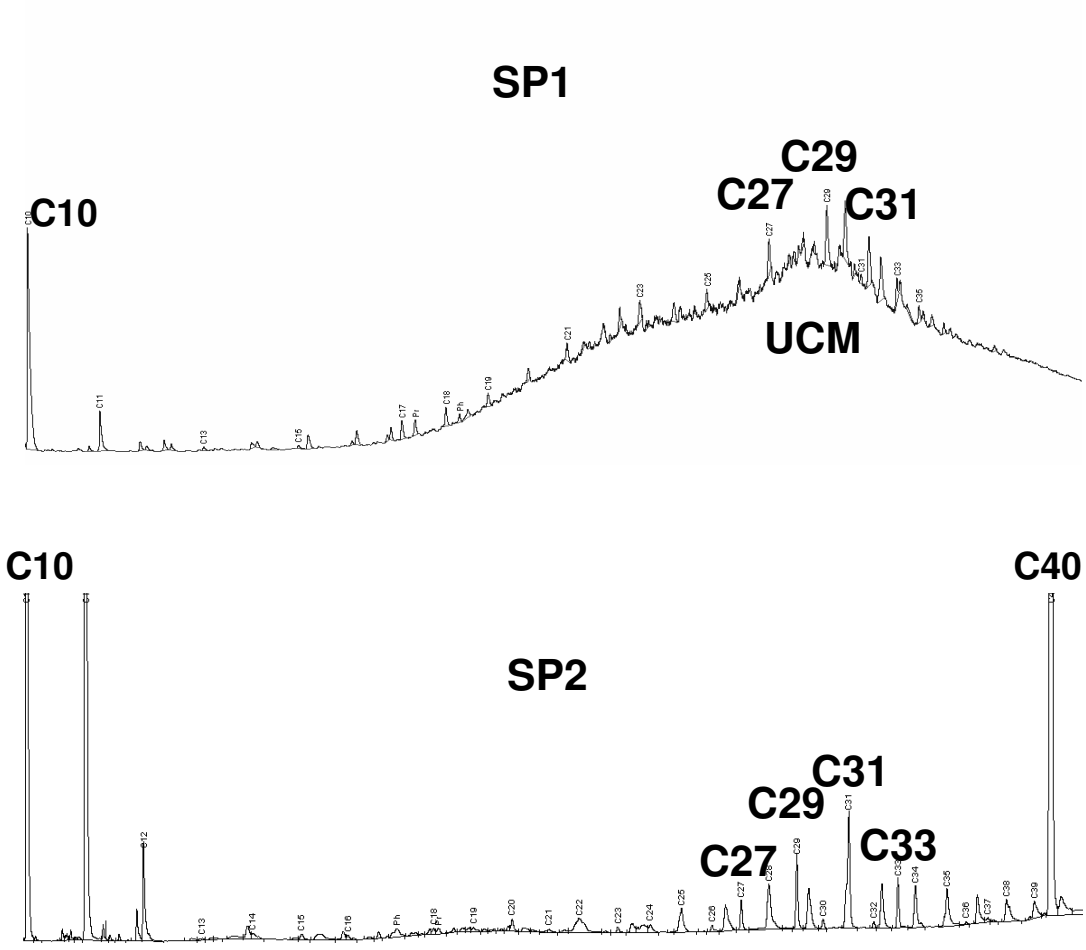


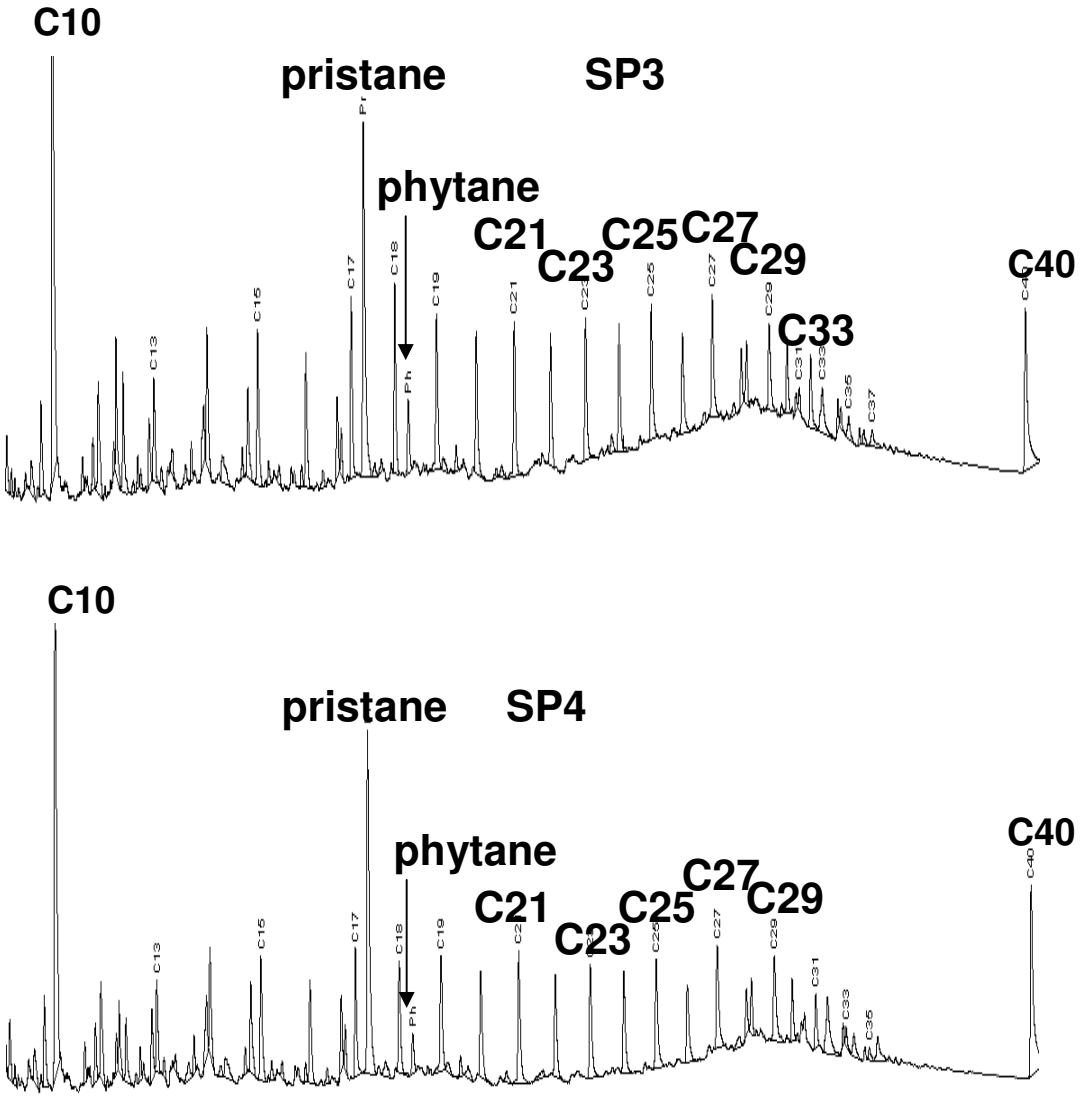
Figure 12: Cross plots a) Ant/Ant+Phe ratio versus Flu/Flu+Py ratio (Yunker et al. 2002), b) $C_0/(C_0+C_1)$ of phenanthrene/(phenanthrene+(C_1 phenanthrene+anthracene)) ratios versus Ant/(Ant+Phe) ratio (Yunker et al. 2002), c) Flu+Py/((Flu+Py)+C_2-C_4 Phe+Ant) (Neff et al. 2005) ratio versus C_1-C_4 Phe+Ant/Phe+Ant ratio (Prahl and Carpenter 1983) for SP1 to SP5 and coals.

Substituted PAHs are distinct tracers for petrogenic PAHs. Low $C_0/(C_0+C_1)$ phenanthrene/anthracene ratios (<0.4) indicate a petrogenic input, ratios >0.5 indicate coal or wood combustion or weathered urban aerosols input (Yunker et al. 2002). Prahl and Carpenter (1983) found that a methylphenanthrene/phenanthrene (methylphenanthrene as the sum of C_1-C_4 alkyl homologues) ratio <1 is characteristic for combustion derived PAHs and ratios between two and six for petrogenic PAHs. Fluoranthene+pyrene/(fluoranthene+pyrene+$C_{2\text{-}4}$ phenanthrene+anthracene) ratios of petrogenic and pyrogenic sources generally exhibit values in the range of zero and one, with the ratio of less than 0.1 for a petrogenic source, and a ratio of more than 0.75 for a pyrogenic PAH source (Neff et al. 2005).

4.3.4 n-Alkanes

The GC-FID chromatogram of SP1 displays a distinct unresolved complex mixture (UCM) (Figure 13), and a CPI value of 1, pristane/phytane ratio was not possible to determine. The pattern of SP2 exhibits no UCM, but intense n-alkane peaks in the C27-C35 range.




C10
pristane
SP3
phytane
C21
C25
C27
C23
C29
C40
C33
C10
pristane
SP4
phytane
C40
C27
C21
C25
C23
C29

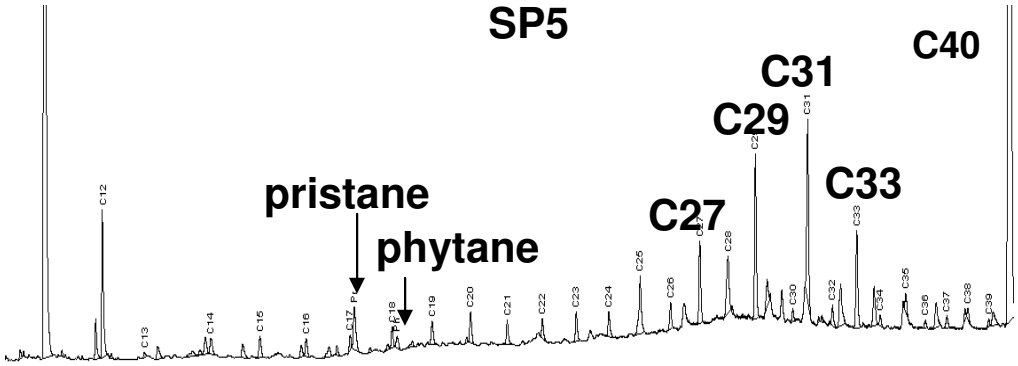


Figure 13: GC-FID n-alkane chromatograms of SP1-SP5.

The soil showed a CPI of 3.3 and a pristane/phytane ratio of 2.5. The GC-FID chromatograms of SP3, SP4 and SP5 showed a slight UCM in the C25 to C37 range and discrete peaks (Figure 13).

The CPI values of the selected soil samples of SP3, SP4 and SP5 were 1.4, 1.5 and 2.9 and the pristane/phytane ratios were 5.7, 8.9 and 3.2, respectively. In this study pristane/phytane ratios of the reference materials (i.e. coals) were 6.4 for the middle volatile bituminous coal and 11.6 for the anthracite, which were similar to the samples collected from SP3 and SP4. The pristane/phytane ratio of the high volatile bituminous coal was not possible to determine. The CPI values for the coals were 0.9 (high volatile bituminous coal), 1 (middle volatile bituminous coal) and 0.9 (anthracite) with similar values observed at SP1, SP3 and SP4. These CPI values are characteristic of oils (petroleum contamination) and high ranked coals (Radke et al. 1980; Wang et al. 1999). Although the PAH distribution pattern suggested a pyrogenic source for SP1, the UCM and CPI values from the analysis of n-alkanes indicated the presence of oil in the soil. Soils and sediments contaminated by oils is often associated with urban runoff or fallout (biodegraded petroleum, uncombusted petroleum, motor and hydraulic oils), and are characterized by an UCM of branched and cyclic alkanes and a broad profile in the C18 to C40 range with nearly no resolved n-alkanes (Gogou et al. 2000; Stout et al. 2001). However, in addition soils could have been impacted by petroleum during flood events from shipping activities and refineries. With n-alkane analyses the presence of coal particles was confirmed

for SP3 and SP4. Both the prominence of the odd alkanes and the remarkable abundance of pristane in the soils indicated a formation from higher plant debris (including fossilized coals). Furthermore, CPI values >5 are characteristic of natural terrestrially-derived hydrocarbons and non-contaminated sediments (Colombo et al. 1989; Sicre et al. 1987). High pristane/phytane ratios are characteristic of biogenic n-alkanes and low ranked coals (ratio 8-11), while low pristane/phytane ratios are the result of oils (ratio <2) and higher ranked coals (ratio <8) (Amijaya 2005; Wang et al. 1999). Thus, the pristane/phytane ratios of SP4 and SP2 were similar to biogenic n-alkanes and low ranked coals, and the pristane/phytane ratios of SP3 and SP5 were similar to higher ranked coals.

4.3.5 PCA

A factor score plot of the first and second principal components derived from the forty five PAHs in Table 5 is shown in Figure 14. PC-1 and PC-2 account for 45.5 and 12.7% of the variability in the data.

The samples collected from SP1 and SP2 are plotted in the same area of the diagram, but are clearly separated from SP3-SP5. The factor score plot of Figure 14a shows a correlation between SP1 and SP2, and also a correlation between SP3-SP5. The chemical causes underlying these relationships can be determined by examining the factor loadings. Figure 14b shows that the four to six ring PAHs are a chemical signature of SP1-SP2 (pyrogenic signature) and the two to three ring PAHs plus the substituted PAHs are the chemical signature of SP3- SP5 (petrogenic signature).

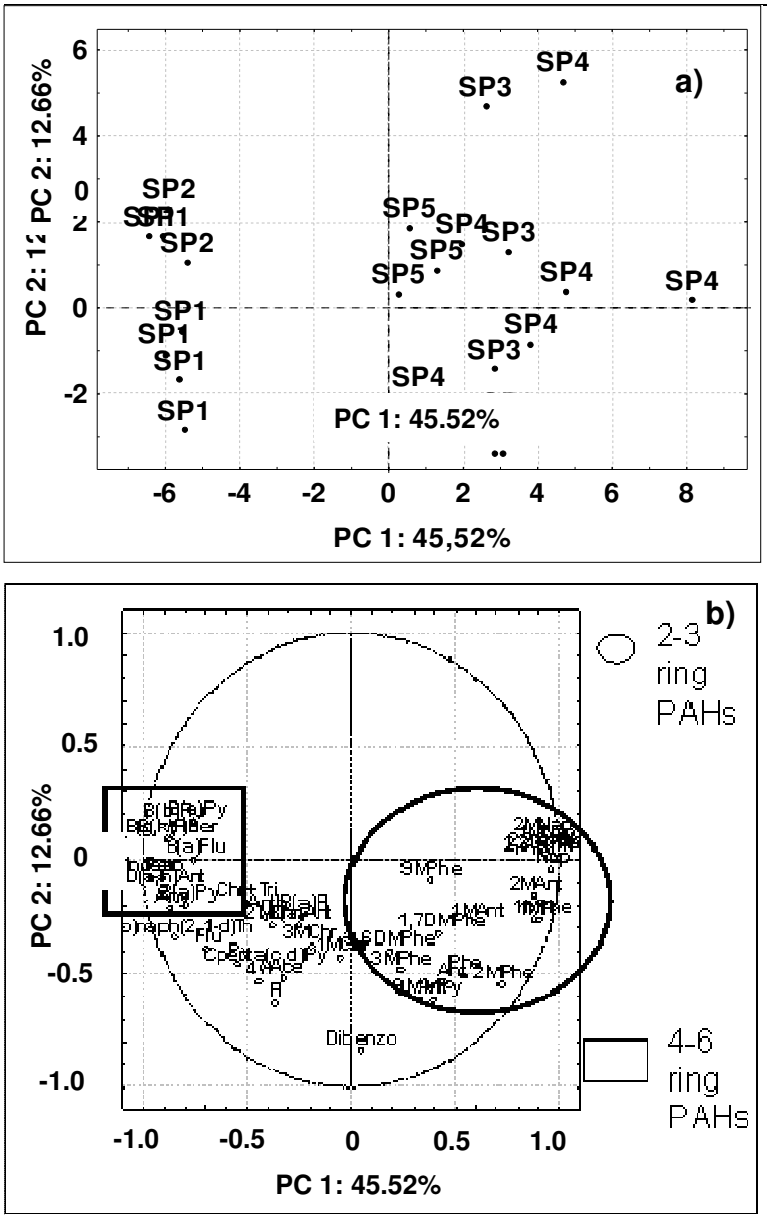


Figure 14: Principal component analysis.

4.4 Conclusions

Source identification of PAHs in environmental matrices (e.g. river bank soils) is complex (Pies et al. 2007). In the present study, the application of different source identification methods concluded that combustion derived PAHs are dominant at SP1 and SP2, with an additional input of lubricating oils identified at SP1. At sampling points SP3-SP5, a mixture of petrogenic and pyrogenic sources is found. In SP3-SP5

coal particles represent the main petrogenic input, with additional information provided from PAH analyses of coal samples collected from the Saarland as reference materials for source identification. This study showed that in complex mixtures the analysis of parent PAHs is beneficial for the identification of pyrogenic sources, while the analysis of n-alkanes is essential to obtain detailed information about the petrogenic source (e.g. weathered lubricating oil). The use of PCA for data analysis also provided a better understanding of the differences between samples and therefore the source of contamination. In summary, sites with diffuse sources of contaminants, like the Mosel sites, are difficult to characterize. Therefore, source identification of complex PAH mixtures requires more than one identification method to identify PAH source(s). Hence, a concept for source identification of bank soils can be proposed: 1) collection of information about site history, 2) use of coal petrography if the samples are impacted by coal mining 3) selection and use of alkylated PAHs (i.e. methylnaphthalenes, methylphenanthrenes -anthracenes, methylfluoranthenes - pyrenes) with respect to distribution patterns and a calculation of PAH ratios, 4) interpretation of n-alkane measurements, 5) use of C_1-C_4 homologue series if data are available and 6) use of PCA.

In the case of the coal impacted study area, additional coal petrography was essential for identifying coal and coal derived particles in the soils. If sources of contaminants can be determined, risk assessment is simpler due to the known characteristics of contaminants. Nevertheless, detailed investigations on sorption, desorption, and bioavailability of soils contaminants are recommendable.

5 Identifying sources of polycyclic aromatic hydrocarbons (PAHs) in soils: Distinguishing point and non-point sources using an extended PAH spectrum and n-alkanes

5.1 Introduction

In chapter four it could be shown that determining the contaminant source is exceedingly difficult when it occurs in a complex environmental mixture (Pies et al. 2008). In general, only combinations of various methods deliver a characteristic source fingerprint. Most of the forensic methods are complex and only useful in combination which make forensic investigations expensive. To save costs one major difficulty is the selection of the appropriate tool or strategy to identify the source, in this case the PAH source. Here, selected samples from point sources and non-point sources were investigated. Three approaches are tested by measuring (1) an extended PAH spectrum (i.e. forty five instead of the common sixteen EPA-PAHs), (2) PAH ratios and (3) n-alkanes to determine if point sources are distinguishable from non-point sources, and if an individual source can be distinguished from a multiple source contaminated site in the study area. A further objective was to evaluate whether these methods are sufficient as the first step toward identifying sources of PAHs in selected samples, and if they allow for superior decision-making before resorting to more expensive methods.

5.2 Material and Methods

5.2.1 Sample description

Eighteen samples with known PAH sources (point sources, which were known to be present in the Mosel and Saar region) were analyzed. The point sources were two gasworks (GW1, GW2, both gasworks samples were gathered from the area of the creosote basins), a tar impregnation facility (TIF), a creosoted timber (CT), an acid tar

derived from purified waste oil (AT), a tank farm (TF) and a diesel contaminated site (D). Additionally, three river bank soils from the Mosel and Saar rivers with known non-point PAH sources (Pies et al. 2008) were investigated. Soil samples were collected using a stainless steel core (Ø 5 cm or Ø 8 cm). Sampling sites were situated before the confluence of the Saar with the Mosel river (Ss1), at the Saar river (Ss2) and after the confluence of the Saar and the Mosel (Ss3) (Figure 5, Ss1 correlates to SP1, Ss2 to SP3 and Ss3 to SP4). Previous studies of river bank soils Ss2 and Ss3 detected coal particles in the soils (Pies et al. 2007; Yang et al. 2008a) and additionally related the PAH content to the coal particles (Yang et al. 2008a). To compare the coal bearing soils of Ss2 and Ss3 to the PAH source coal, nine samples of raw coal from Saar and Ruhr mining areas were studied: an anthracite (Ant), three high volatile bituminous coals (HVBC1-3), three hard coals (HC1-3), a fat coal (FC) and a medium volatile bituminous coal (MVBC). Due to detection limits, only soil samples with relatively high PAH concentrations (>20 mg kg^{-1} for the sixteen EPA PAHs) were used to determine the concentrations of the Σ_{45} PAHs and n-alkanes.

Table 7: Sampling sites and materials including data on source, characteristics and concentrations of sixteen EPA PAHs and all the 45 analyzed PAHs (in mg kg^{-1})

	GW1	GW2	TIF	D	TF	AT	CT	Ant	HVBC1	HVBC 2
Sampling site	Idar-Oberstein	Bernkastel-Kues	Neumagen-Dhron	Traben-Trarbach	Bad-Kreuznach	Gau-Algesheim	Old vineyard	Coal mining (Saarland)	Coal mining (Saarland)	Coal mining (Ruhr area)
Soil/ Material	Coarse	Coarse	Sandy-Coarse	Coarse	Coarse	Tar, viscous	Wood	Coal	Coal	Coal
Characteristics	Black, tar smell	Black, tar smell (area of the former tar pit)	Silver-grayish, tar smell	Odorless	Distinct smell	Black, tar smell	Black, tar smell	Black, shiny	Black, shiny	Black, shiny
Sampling depth [m]	5.4	1	2-3		3	Surface	-	-	-	-
Σ_{16} EPA PAH	760	1189	769	0.5	8.5	4290	142918	0.7	50	6
Σ_{45} PAH	1014	1583	1036	1.1	37	5932	186738	1.1	170	24

	HVBC 3	HC 1	HC 2	HC 3	FC	MVBC	Ss1	Ss2	Ss3
Sampling site	Coal mining (Saarland)	Unknown	Coal mining (Ruhr area)	Coal mining (Saarland)	Coal mining (Saarland)	Unknown	Bank soil of Mosel River	Bank soil of Saar River	Bank soil of Mosel River
Soil/ Material	Coal	Coal	Coal	Coal	Coal	Coal	Sand/Silt	Sand/Silt	Sand/Silt
Character-istics	Black, shiny	Black, shiny	Black, shiny	Black, shiny	Black, shiny	Black, shiny	Odorless	Odorless, coal bearing	Odorless, coal bearing
Sampling depth [m]	-	-	-	-	-	-	0-2	0-1.40	0-1
Σ_{16} EPA PAH	13	29	10	22	37	22	31-84	30-128	35-89
Σ_{45} PAH	53	130	68	85	131	69	43-114	50-197	53-158

(GW 1-2: gasworks 1-2, TIF: tar impregnation facility, D: diesel contamination, TF: tank farm, AT: acid tar, CT: creosoted timber, Ss 1-3: soil samples of sampling site 1-3, Ant: anthracite, HVBC 1-3: high volatile bituminous coal 1-3, HC 1-3: hard coal 1-3, FC: fat coal, MVBC: medium volatile bituminous coal)

Detailed information on the sampling sites and samples is given in Table 7. The location of the sampling sites Ss1 to Ss3 are displayed in Figure 5 of chapter 2 (in Figure 3 Ss1 correlate to SP1, SS2 to SP3 and Ss3 to SP4)

5.2.2 Sample preparation and analyses

Coal samples and soils were homogenized after sampling, freeze dried, grinded to < 2 mm and extracted with a hexane/acetone solution (2:1) via Pressurized Liquid Extraction (PLE). The gaswork 1 and gaswork 2 samples (each 10 g) were extracted when wet. A mass of 10 to 15 g of the wet tar impregnation facility, and diesel samples were prepared according to DIN ISO 16703 via shaking extraction with a heptane/acetone solution (2:1) and sonication. Water was removed by adding sodium sulfate. Soxhlet extraction, for 6 hours, using a hexane/acetone solution (2:1) was used for creosoted timber (0.5 g splinters of wood) and acid tar samples (1.5 g of tar). To avoid loss of high volatile substances during sampling, 52 g of tank farm sample were put directly into a bottle, filled with a hexane/acetone solution (2:1) and extracted according to DIN ISO 16703. In all samples, acetone was evaporated with a gentle nitrogen stream. Clean up and analyses by a gas chromatograph coupled to a mass spectrometer (GC-MS, Agilent GC 6890N, MSD 5975) were performed according to Pies et al. (2008). Internal standard surrogates were spiked into the

concentrated extracts prior to clean up, and included naphthalene d8, acenaphthylene d8, phenanthrene d10, fluoranthene d10, pyrene d10, benzo(a)pyrene d12 and benzo(g,h,i)perylene d12 (LGC Promochem GmbH Wesel, Germany). Target compounds are identified in Table 8. The extracts were eluted with hexane and concentrated with N_2 to approximately 1 ml. For GC-MS analyses a volume of 1 µl was injected in splitless mode and a HP 5-MS (phenyl-methyl-siloxane) column with 30 m x 0.25 mm ID, 0.25 µm film thickness was used. The mass spectrometer was operated with selected ion monitoring mode (SIM). The analyzed substances are listed in Table 8.

Clean up for n-alkane analyses was carried out according to DIN ISO 16703 with Florisil columns.

Prior to clean up samples were spiked with n-decane (C_{10}; 30 µl l^{-1}), n-undecane (C_{11}; 30 µl l^{-1}) and n-tetracontane (C_{40}; 30 mg l^{-1}). Samples were analyzed by a gas chromatograph equipped with a flame ionization detector (GC-FID, Chrompack 9002).

Table 8: Analyzed PAHs (EPA-PAH with check mark).

PAH		PAH	
Naphthalene (Nap)	✓	Benzo(a)fluorene (B(a)fl	
2-Methylnaphthalene (2MNap)		1Methylpyrene (1MPy)	
1-Methylnaphthalene (1MNap)		Benzo(b)naphtho(2,1-d)thiophene (B(b)naph(2,1-d)th)	
2,3-Dimethylnaphthalene (2,3DMNap)		Cyclopenta(cd)pyrene (Cpenta(cd)Py)	
Acenaphthylene (Any)	✓	Benzo(a)Anthracene (B(a)Ant)	✓
1,2-Dimethylnaphthalene (1,2DMNap)		Chrysene+Triphenylene (Chr+Tri)	✓
Acenaphthene (Ace)	✓	3-Methylchrysene (3MChr)	
2,3,5-Trimethylnaphthalene (2,3,5TMNap)		2-Methylchrysene (2MChr)	
Fluorene (Fl)	✓	5-Methylchrysene (5MChr)	
1-Methylfluorene (1MFl)		1-Methylchrysene (1MChr)	
Dibenzothiophene (Dibenzo)		Benzo(b)fluoranthene (B(b)Flu)	✓
Phenanthrene (Phe)	✓	Benzo(k)fluoranthene (B(k)Flu)	✓
Anthracene (Ant)	✓	Benzo(a)fluoranthene (B(a)Flu)	
3-Methylphenanthrene (3MPhe)		Benzo(e)pyrene (B(e)Py)	
2-Methylphenanthrene (2MPhe)		Benzo(a)pyrene (B(a)Py)	✓
2-Methylanthracene (2MAnt)		Perylene (Per)	
1-Methylanthracene+9-Methylphenanthrene (1MPhe+9MPhe)		Indeno(1,2,3-cd)pyrene (Indeno)	✓
1-Methylphenanthrene (1MPhe)		Dibenzo(ah)Anthracene (D(ah)Ant)	✓
9-Methylanthracene (9MAnt)		Benzo(ghi)perylene (B(ghi)Per)	✓
3,6-Dimethylphenanthrene (3,6DMPhe)		Anthanthrene (Anth)	
1,7-Dimethylphenanthrene (1,7DMPhe)			
Fluoranthene (Flu)	✓		
Pyrene (Py)	✓		

5.3 Results

5.3.1 PAH pattern

For most point source samples, the Σ_{16} PAHs were the dominant compounds (Σ_{16} PAH >60% to total PAHs) (see Table 7).

Point sources containing tar or coal tar derived creosote (gasworks, tar impregnation facility, creosoted timber, acid tar) showed a similar PAH mixture. They consisted primarily of three to four ring PAHs. Differences were apparent in gasworks samples, for example, naphthalene was the most abundant component, while benz(a)pyrene occurred at high concentrations in the same samples (see Figure 15 A,B).

Alkylated PAHs were significantly present in diesel, tank farm and coal samples (Σ_{16} PAH <50% of total PAHs) (see Table 7). The diesel contaminated sample exhibited a distinct abundance of high molecular weight (HMW) PAHs, especially benz(a)pyrene. The sample was dominated by pyrene, but also by an elevated percentage of alkylated phenanthrene.

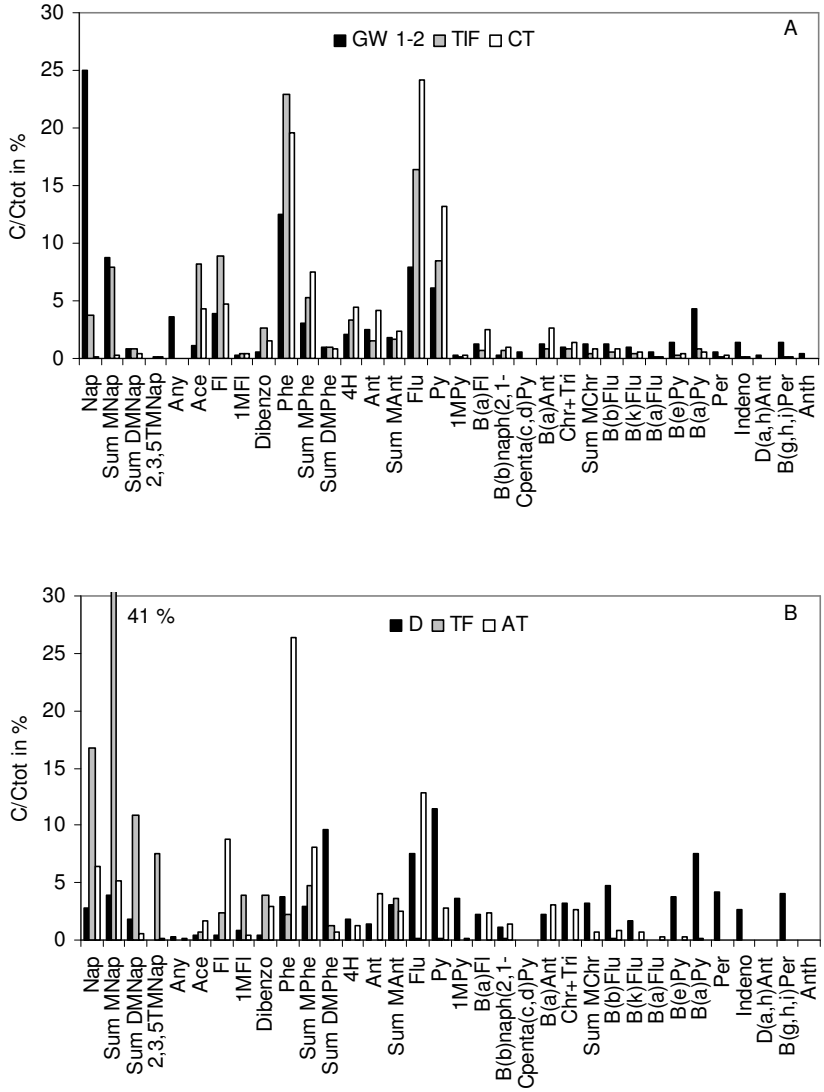
Tank farm sample showed an individual pattern with high naphthalene concentrations, especially methylnaphthalene and other volatile PAHs. Alkylated PAHs were more abundant than parent PAHs, which is characteristic of fuels.

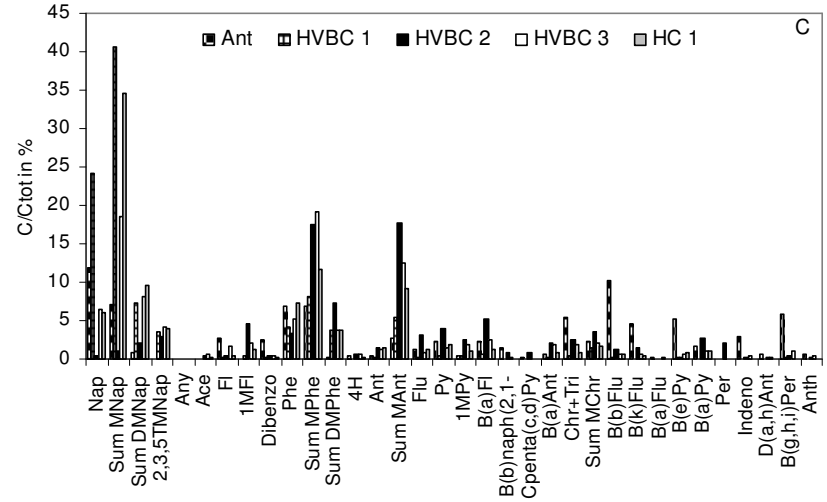
Coal samples had the same distribution patterns when compared to each other. High molecular weight PAHs were of minor significance except for Ant, while benzo(b)fluoranthene, benz(e)pyrene and benz(ghi)perylene showed a higher abundance in these samples. High levels of alkylated PAHs, in comparison to parent PAHs, were characteristic of coal samples (see Figure 15 C,D).

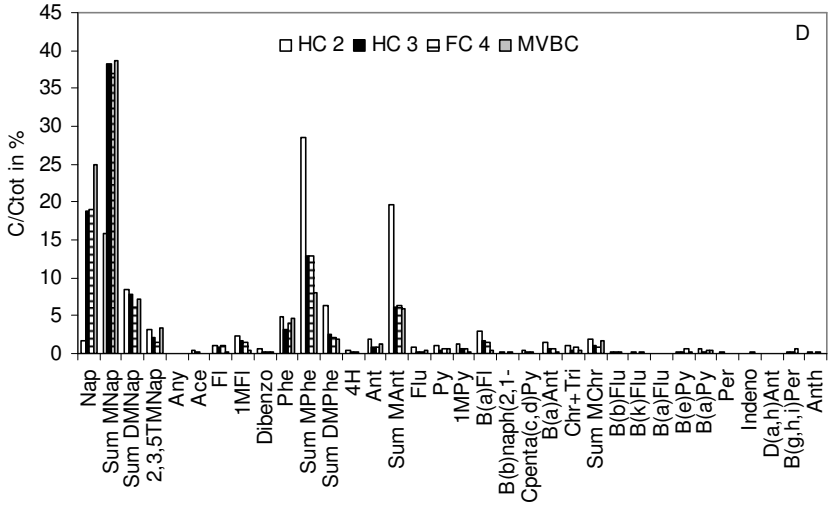
The Σ_{16} EPA PAHs contributed most to non-point sources in Ss1. Samples were dominated by fluoranthene, pyrene and high molecular weight PAHs
(see Figure 15 E).

Phenanthrene contributed to a higher amount of total PAHs than other low molecular PAHs. Soils Ss2 and Ss3 showed similar distribution patterns. Alkylated PAHs such as methylnaphthalenes and phenanthrenes were more abundant than samples

collected from Ss1 (see Figure 15 E). Since the distribution patterns of all soil samples for each site were similar, only one sample is displayed as representative.




C
Ant
HVBC 1
HVBC 2
HVBC 3
HC 1
C/Ctot in %
0
5
10
15
20
25
30
35
40
45
Nap
Sum MNap
Sum DMNap
2,3,5TMNap
Any
Ace
Fl
1MFl
Dibenzo
Phe
Sum MPhe
Sum DMPhe
4H
Ant
Sum MAnt
Flu
Py
1MPy
B(a)Fl
B(b)naph(2,1-
Cpenta(c,d)Py
B(a)Ant
Chr+Tri
Sum MChr
B(b)Flu
B(k)Flu
B(a)Flu
B(e)Py
B(a)Py
Per
Indeno
D(a,h)Ant
B(g,h,i)Per
Anth


D
HC 2
HC 3
FC 4
MVBC
C/Ctot in %
0
5
10
15
20
25
30
35
40
45
Nap
Sum MNap
Sum DMNap
2,3,5TMNap
Any
Ace
Fl
1MFl
Dibenzo
Phe
Sum MPhe
Sum DMPhe
4H
Ant
Sum MAnt
Flu
Py
1MPy
B(a)Fl
B(b)naph(2,1-
Cpenta(c,d)Py
B(a)Ant
Chr+Tri
Sum MChr
B(b)Flu
B(k)Flu
B(a)Flu
B(e)Py
B(a)Py
Per
Indeno
D(a,h)Ant
B(g,h,i)Per
Anth

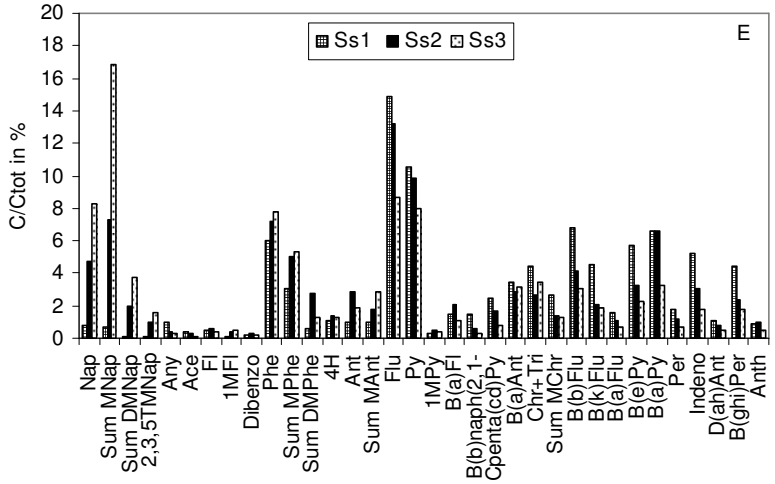


Figure 15: PAH distribution patterns of samples from known sources (A,B), coals (C,D), and soil samples of Ss1-Ss3 (E-G) with the percentage of the individual substance to the total PAH concentration (C/Ctot).

5.3.2 PAH ratios

Due to the importance of alkylated PAHs, two ratio plots were used: the fluoranthene/pyrene to phenanthrene/anthracene ratio (Figure 16 A) and the C0/(C0+C1) (phenanthrene and anthracene) to fluoranthene/(fluoranthene + pyrene) ratio (Figure 16 B).

Results of PAH ratios for gaswork, creosoted timber, and acid tar samples indicated that the source was pyrogenic (i.e., formed by combustion). The ratio fluoranthene/pyrene to phenanthrene/anthracene from diesel indicates petroleum combustion and the C0/(C0+C1) (phenanthrene and anthracene) to fluoranthene/(fluoranthene + pyrene) ratio also inferred petroleum as the source. The tank farm sample could not be calculated because anthracene was not detected. The tar impregnation facility sample plotted within the petroleum source section in cross plot 16 A and within the combustion section in cross plot 16 B (see Figure 16). The coal samples revealed a wide range for all ratios used. Coal samples anthracite, hard coal 3, fat coal, high volatile bituminous coal 1 and high volatile bituminous coal 3 fell within the petroleum source section (refer to cross plot of Figure 16 A). In contrast,

ratios of the high volatile bituminous coal 2, hard coal 1, hard coal 2 and medium volatile bituminous coal occurred in the section of petroleum combustion. In the cross plot displayed in Figure 16 B, coal samples anthracite, hard coal 3, fat coal and high volatile bituminous coal 3 fell within the petroleum section. The result is similar to that of the cross plot in Figure 16 A. All soil samples were within the combustion section of the cross plot in Figure 16 A. In contrast to the cross plot in Figure 16 A, the coal particle containing soils of Ss2 and Ss3 inferred a petrogenic influence in four samples of Ss2 and all samples for Ss3 in cross plot B (Figure 16 B).

The results of PAH ratios brought to light discrepancies between cross plots A and B for samples collected from tar impregnation facility, diesel, four samples of Ss2 and all samples of Ss3 (i.e., depending on the ratios calculated, the distribution plot shifted to either identifying the source as combustion or petrogenic.

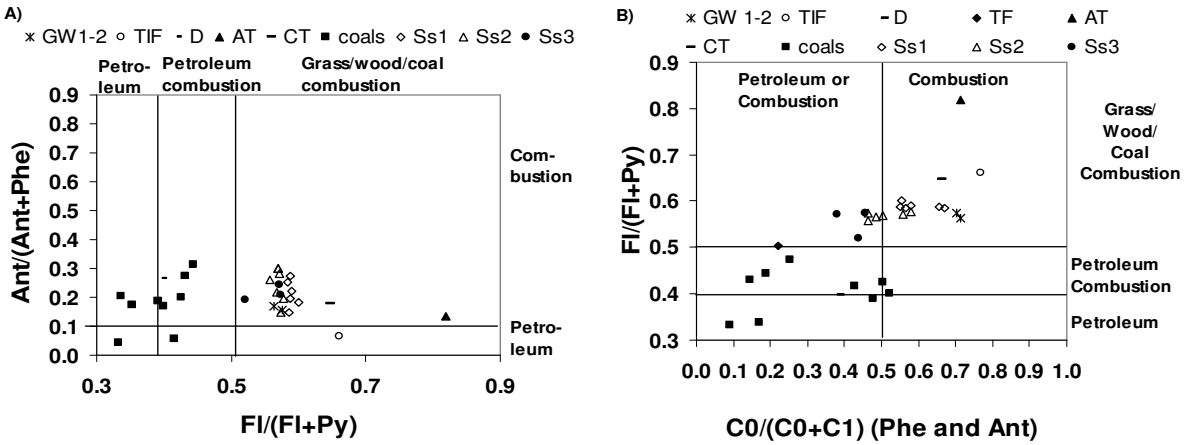
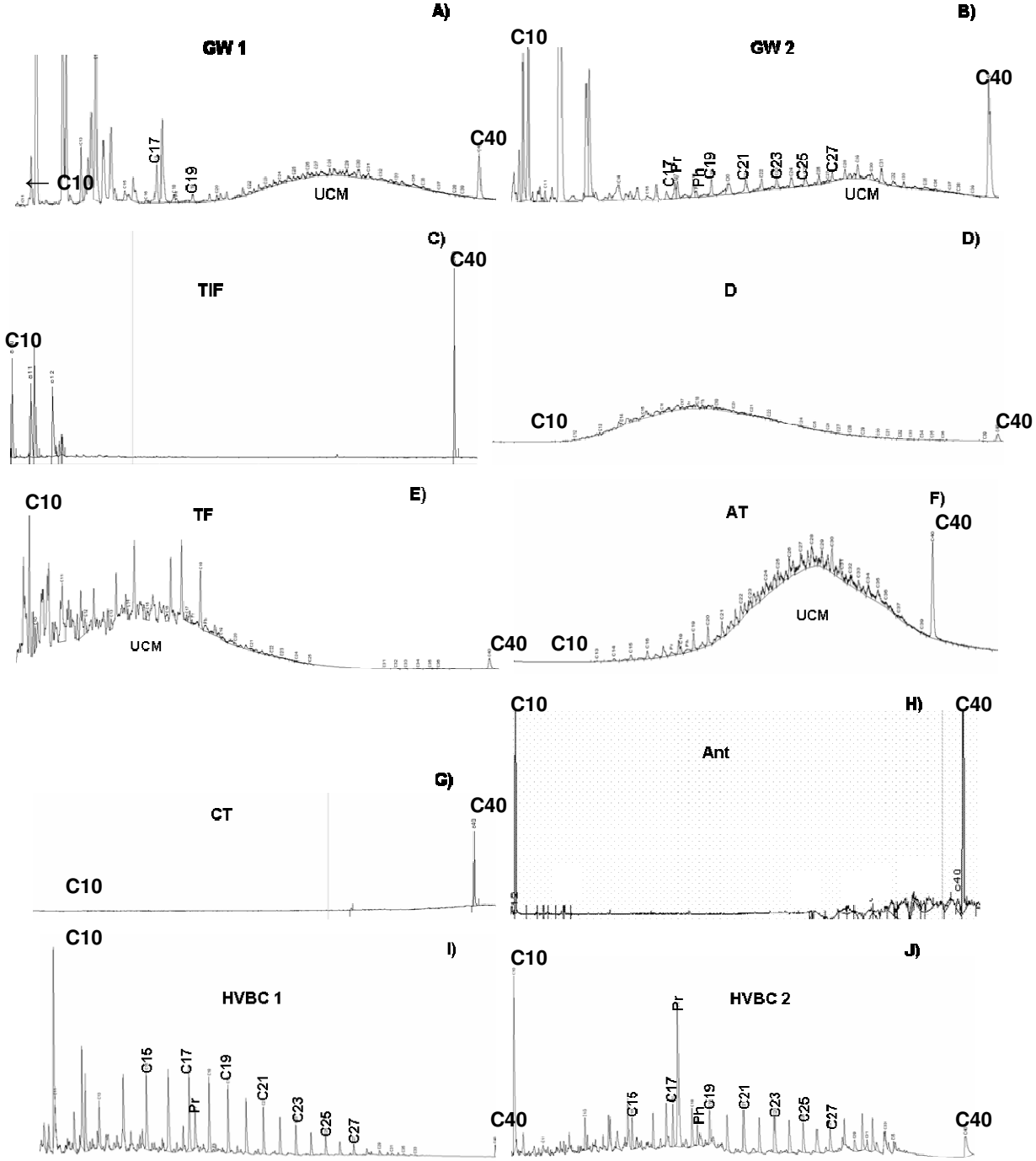


Figure 16: Cross plot A) of the Ant/(Ant+Phe) ratio against the Flu/(Flu+Py) ratio (Yunker et al. 2002) and B) of the $C_0/(C_0+C_1)$ of phenanthrene + anthracene ratios against the Ant/(Ant+Phe) ratio (Yunker et al. 2002) for the studied samples.

5.3.3 n-Alkanes

n-Alkane distributions varied among all investigated samples. The sample gaswork 1 revealed an unresolved complex mixture (UCM) ranging from C21–C36. It showed no distinct n-alkane peaks in the C21–C36 range (Figure 17 A). In contrast, GW2

yielded discrete small peaks (Figure 17 B) with a carbon preference index (CPI) of 1.2, a C17/pristane ratio of 0.8 and a C18/phytane ratio of 2.4. Samples of tar impregnation facility and creosoted timber produced no n-alkane peaks (Figure 17 C, Figure 17 G).



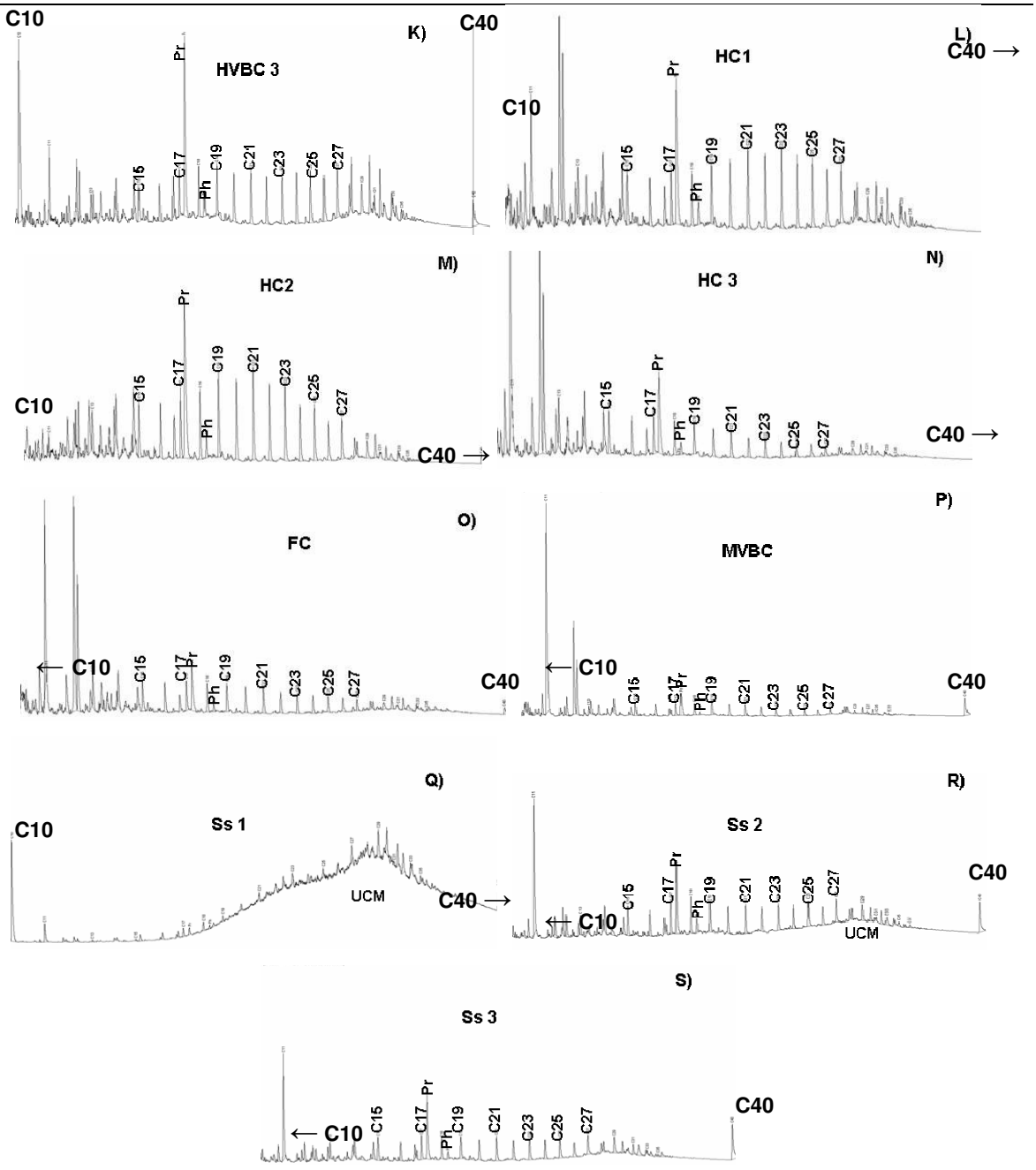


Figure 17: n-Alkane distributions of contaminated soils and materials from known sources (A-G), coals (H-P) and contaminated bank soils from known sources (Q-S) (Ss1-3).

The diesel sample displayed a hydrocarbon distribution with an UCM peak in the C12-C28 range and nearly no n-alkane peaks (Figure 17 D). The tank farm sample exhibited a distribution with an UCM peak in the C11–C22 range with discrete peaks closer to the volatile hydrocarbon range (Figure 17 E). n-Alkane distribution of the

acid tar site demonstrated a clear UCM peak in the C20–C39 range with no discrete peaks (Figure 17 F).

All studied coals exhibited discrete peaks in the C15–C29 range, except anthracite (Figure 17 H–Figure 17 P). The presence of pristane was dominant in high volatile bituminous coal 2, high volatile bituminous coal 3, hard coal 1, hard coal 2, hard coal 3 and fat coal. CPI values of coals ranged from 1.0 to 1.4 indicating a slight preponderance of odd carbon n-alkanes (except anthracite, which has no n-alkanes).

Analyses of n-alkanes of Ss1 demonstrated a distinct UCM hump in the range of C17-C38 with a CPI value around 1 (Figure 17 Q). Patterns of Ss2 and Ss3 showed a slight UCM hump in the C25–C37 range and discrete peaks (Figure 17 R–Figure 17 S). Odd carbon n-alkanes were more abundant than even carbon n-alkanes.

5.4 Discussion

5.4.1 PAH Pattern

Samples of tar impregnation facility, creosoted timber and acid tar were difficult to distinguish with the use of PAH patterns since they were similar to each other (tar and coal tar derived creosote is the petrogenic PAH source of these samples). In contrast to other studies investigating the presence of PAHs in tar products, the samples used in this study failed to exhibit the expected PAH pattern, especially the elevated naphthalene concentrations (Brown et al. 2006; Wise et al. 1988). Usually, low molecular weight PAHs with only two or three fused benzene rings, as well as alkylated homologues, are the major constituents of petroleum (Fernandes et al. 1997), while alkylated PAHs are more abundant than parent PAHs (Sporstöl et al. 1983; Stout et al. 2002a).

Although the gaswork samples contained creosote components and showed similar patterns to tar impregnation facility, creosoted timber and acid tar samples, they nonetheless exhibited high naphthalene content, which is in agreement with other studies (Fiedler et al. 1997; Saber et al. 2006; Stupp and Püttmann 2001). Since naphthalene is the most volatile PAH and the first component which disappears when

exposed to environment or to pyrogenic processes, weathering must be the reason for the absence of naphthalene in samples tar impregnation facility, creosoted timber and acid tar. In accordance with this explanation, the samples containing tar and coal tar derived creosote showed typical PAH patterns (see Figure 15).

Samples contaminated with gasoline (tank farm) or diesel (diesel) showed pronounced differences to other investigated samples (i.e., higher abundance of alkylated PAHs for tank farm and higher abundance of high molecular weight PAHs for diesel) and are distinguishable from other PAH sources (see Figure 15).

The high proportion of alkylated PAHs of investigated coal samples was characteristic for these samples. This PAH pattern was described as an indicator for a petrogenic source (Youngblood and Blumer 1975). Previously, other authors reported high contents of naphthalene, phenanthrene and their alkylated derivatives in coal samples (Amijaya 2005; Stout et al. 2002a). Despite their different maturity, the investigated coal samples revealed similar PAH patterns and can be distinguished from other samples.

Soil samples of Ss1 were dominated by four to six ring PAHs, which are typical for traffic emissions (Rehwagen et al. 2005). Additionally, high molecular weight PAHs with four to six rings were generated mainly by incomplete combustion of organic matter, inferring the presence of pyrogenic PAHs (e.g. fluoranthene, pyrene, benzo(ghi)perylene) (Fernandes et al. 1997).

As previously described in Pies et al. (2007, sample SP1), the PAH distribution pattern of Ss1 denotes a pyrogenic contamination without petrogenic input. Samples Ss2 and Ss3 exhibited similar PAH patterns, indicating a common source. Based on coal petrography for Ss2 and Ss3 (Yang et al. 2008a; Yang et al. 2008b) and the distribution patterns of investigated coals, the authors concluded that naphthalenes arise from coal particles in the soils. However, the high content of high molecular weight PAHs argues for a possible atmospheric input. Therefore, a mixture of pyrogenic and petrogenic PAHs were found at Ss2 and Ss3.

The present study demonstrated that by using an extended PAH spectrum, it is possible to fingerprint and distinguish sources of contamination. In addition, the use

of alkylated PAHs is considered essential for identifying petrogenic sources (e.g. coal, oils), especially regarding non-point sources where the sole use of common sixteen EPA PAHs is unhelpful with source identification.

5.4.2 PAH Ratios

Separating petrogenic and pyrogenic sources is commonly accomplished by calculating the PAH ratios, such as phenanthrene/anthracene and fluoranthene/pyrene (Budzinski et al. 1997; Gschwend and Hites 1981; Sicre et al. 1987). In cross plots A and B (see Figure 16), tar impregnation facility, creosoted timber and acid tar samples showed widely different PAH ratios in comparison to other samples. In contrast to the similarity among the PAH patterns, the PAH ratios of these samples were not comparable. All samples, except tar impregnation facility, diesel, Ss2 and Ss3, showed consistency between their source and calculated PAH ratios. Depending on the ratio used, different sources were indicated for the tar impregnation facility, diesel, Ss2 and Ss3 samples. When alkylated PAHs were included in the calculation of PAH ratios, the tar impregnation facility sample shifted to the combustion zone, diesel sample to the petroleum zone and Ss2 and Ss3 samples to the petroleum or combustion zone. These changes point to a non-point source for soil samples, as well as for the presence of pyrogenic compounds in diesel and tar impregnation facility samples.

PAH ratios of coal samples were ambiguous and resulted in a number of possible interpretations. Coal samples plotted in the petroleum section, as well as in the petroleum combustion section.

Ratios with parent PAHs failed to provide accurate source identification of PAHs, especially for non-point sources. Source identification using PAH ratios was only reliable if both parent and alkylated PAHs were measured. A former study using a multimedia approach recommended the use of high molecular weight PAH ratios such as indeno(1,2,3-cd)pyrene/benzo(ghi)perylene which is more resistant to degradation processes during the transport from source to receptor (Zhang et al.

2005). However, the results of the present study obtained by the ratios of high molecular weight PAHs are neither different nor superior to those obtained by the ratios of phenanthrene/anthracene and fluoranthene/pyrene.

5.4.3 n-Alkanes

A CPI was used when comparing the distribution of n-alkanes with odd and even carbon numbers. It provides information about biogenic/terrestrial and petroleum inputs, as well as pristane/phytane ratios, C17/pristane and C18/phytane ratios and n-alkane patterns (Colombo et al. 1989; Stout et al. 2001; Tolosa et al. 2004; Wu et al. 2007; Yunker and Macdonald 2003).

Weathered oils are characterized by a broad profile in the C18–C40 range with nearly no resolved n-alkane peaks (Wang and Fingas 2003), hence the absence of distinct n-alkane peaks in the C21–C36 range (see Figure 17 A) of gaswork 1 indicated a contamination with heavy weathered oils. The Gaswork 2 sample showed discrete small peaks. CPI, C17/pristane ratio and C18/phytane ratios revealed contamination by oils and a slight degradation of the sample (see Figure 17 B). A CPI value around 1 is characteristic of oils and high ranked coals, while a CPI value >5 is characteristic of natural terrestrially-derived hydrocarbons and non-contaminated sediments (Radke et al. 1980; Sicre et al. 1987). n-Alkane distribution of the tar impregnation facility demonstrated that it only contained high boiling point alkanes, which could not be detected by GC-FID (see Figure 17 C).

The hydrocarbon pattern of diesel displayed an n-alkane distribution of a heavy weathered diesel with an UCM hump in the C12–C28 range and nearly no alkane peaks (Wang and Fingas 2003) (see Figure 17 D). The tank farm sample attested to the presence of gasoline and kerosene (see Figure 17 E), and the sample of acid tar showed a distinct UCM hump indicating heavy weathering of oils (see Figure 17 F). The pattern of n-alkane distribution is characteristic for processed waste oil.

Coal samples exhibited a distinct abundance of pristane (except anthracite, high volatile bituminous coal 1 and medium volatile bituminous coal), which is typical for

low to middle ranked coals (Amijaya 2005; Kaplan et al. 2001) (see Figure 17 H–Figure 17 P). The shift from a n-alkane distribution with a high number of carbon atoms to a distribution with fewer carbon atoms (a heavy-end to a front biased n-alkane distribution) and the disappearance of odd/even n-alkanes, resulted in an increasing rank of coals (Radke et al. 1980) (see Figure 17 I). The anthracite sample showed no peaks which indicates the presence of non-extractable hydrocarbons (see Figure 17 H).

The n-alkane pattern of Ss1 denotes a contamination with highly weathered lubricating oil which is confirmed by a CPI value of 1 (see Figure 17 Q). Due to degradation of the sample, it was difficult to determine a reliable CPI value, therefore the CPI should be used with caution. The presence of discrete n-alkane peaks, the abundance of pristane and a slight UCM hump indicate that parts of the samples Ss1 and Ss2 are the result of higher plant debris (i.e. derived from coal). The C17/pristane ratios of 0.4 and 0.3 and C18/phytane ratios of 2.2 and 2.4 for samples Ss2 and Ss3 also indicate that the source of PAHs is coal particles in the soil. CPI values of 1.4 and 1.5 for these soil samples are similar to CPI values of low to high ranked coals investigated by Amijaya (2005) and Radke et al. (1980) and coals of the present study.

n-Alkane analyses provide more detailed information about petrogenic sources by verifying the presence of oils, diesel, gasoline or coal in non-point sources, as well as in raw materials. Without the n-alkane analysis, degraded oil residues in Ss1 would have been overlooked.

5.5 Conclusions

The extended PAH spectrum including alkylated PAHs allows for the identification of petrogenic inputs which otherwise would not have been possible using only the sixteen EPA PAHs (e.g., for Ss2, Ss3 and coals). Due to a shift from a pyrogenic to a petrogenic source (e.g., non-point source samples Ss2 and Ss3), the PAH ratios are only helpful in characterizing samples (petrogenic vs. pyrogenic), if they are not

derived from more than one potential source. Ratios can provide a source identification by confirming the results of the PAH patterns, as long as alkylated PAHs are included. Alkylated PAHs are essential for the identification of petrogenic sources as demonstrated in the Ss2 and Ss3 samples.

The present research concludes that using an extended, but easy to analyze, PAH spectrum can serve as a valuable first step toward source identification. The presence or absence of alkylated PAHs indicate that either a petrogenic or a non-petrogenic sample (e.g., coals for petrogenic samples) or a petrogenic/pyrogenic input has occurred to environmental samples (e.g., Ss2 and Ss3 for petrogenic inputs and Ss1 for pyrogenic inputs). The methodology tested here simplifies the decision process about which forensic methods should be additionally used to obtain more detailed source identification. For example, if a petrogenic source is predicted by the PAH patterns and the PAH ratios, the analysis of n-alkanes would be helpful to specify the petrogenic source and should be used. In this study n-alkane patterns of Ss2 and Ss3 clearly showed the input of coal particles. The PAH patterns alone only indicate the petrogenic input, but analysis of the n-alkanes could specify the petrogenic input. To confirm a petrogenic source, an alkyl homologue series could be analyzed. The alkyl distribution of petrogenic materials shows a characteristic bell-curve with respect to the degree of alkylation (Murphy and Morrison 2002).

Degradation processes are common in environmental samples and were evident in the diesel and gaswork samples. The next step is to analyze the degradation processes of biomarkers such as terpanes and steranes, isoalkanes and isoprenoids, as suggested by Connan (1984). Once the dominant PAH source characteristics are determined, analysis of the isotopes can proceed. Carbon isotopic ratios of individual PAH can discriminate between inputs of PAHs to the environment in individual depositional systems (O'Malley et al. 1994). However, complete analysis is only necessary if one wants to identify the exact sources. In most cases, the three methods applied in this study are sufficient.

5.6 Recommendation and Perspective

To achieve an accurate source determination, the use of various forensic methods is essential. Determination of PAH alkyl homologue series, biomarkers and isotopes are often recommended (Kaplan et al. 1997; Kaplan et al. 2001; Oros and Simoneit 2000; Wang and Fingas 2003). However, these methods are complex and expensive. This study shows that three relatively simple methods are sufficient for a primary source identification of the investigated samples and to help direct further analytical steps. We therefore recommend the initial use of an extended PAH spectrum since it is cost effective and uncomplicated to analyze, before resorting to additional and expensive forensic investigations. Additional research with an extended sample set should be carried out to validate these findings for other sources and sites.

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6 Mutagenic potential of PAHs in sediments and soils – low impact of coal derived PAHs

6.1 Introduction

A couple of PAHs are identified to exhibit mutagenic and carcinogenic potentials, therefore they are widely studied for potential environmental effects (Fang et al. 2004; Hawthorne et al. 2006; Loibner et al. 2003; Neff et al. 2005; Olajire et al. 2005). They have gained serious attention due to their considerable environmental persistence, toxic potential, high levels of bioaccumulation and harmful biological effects, such as narcosis, genetic mutations and cancer (Baumard et al. 1998; Braga et al. 1999; Durant et al. 1999; Otero-Lobato et al. 2005).

The conversion to metabolites such as dihydrodiol epoxides in an organism lead PAH compounds be genotoxic. They bind covalently to DNA (and RNA) and disrupt them, which is an initiation step in tumour formation (Harvey and Geacintov 1988; Wild and Jones 1995). The best known PAH to induce cancer represents benz(a)pyrene, first identified as potential carcinogen in coal tar by Cook et al. in 1933 (Cook et al. 1933). Other mutagenic or carcinogenic acting PAHs are mostly four to seven ring compounds, especially benzofluoranthenes, benz(a)anthracene, dibenz(ah)anthracene, indeno(1,2,3-cd)pyrene and dibenzopyrenes (IARC 1983).

United States Environmental Protection Agency (US EPA) has identified sixteen PAHs as “priority pollutants” (US EPA 1989) excepting dibenzopyrenes. In addition, there are hundreds of PAH compounds, including alkylated substitutes, which should be considered for risk assessment (Barron and Holder 2003; Neff et al. 2005). However, the European Water Directive only defines seven PAHs as priority pollutants (i.e. naphthalene, fluoranthene, benz(a)pyrene, benz(b)fluoranthene, benz(k)fluoranthene, indeno(1,2,3-cd)pyrene and benz(ghi)perylene) (Parliament 2000).

The aim of this chapter was to elucidate PAH concentrations in coal particle containing soils and in mainly pyrogenic PAH containing soils and sediments of Mosel River. Furthermore, the soils and sediments should be evaluated by

investigating their genotoxic potential with a fluctuation version of the Ames-Test (Reifferscheid et al. 2005).

6.2 Material and methods

6.2.1 Sample preparation and chemical analyses

Two bank soil samples (BS) were gathered with a stainless steel corer (Ø 8 cm) and one sediment sample (SS) with a grab sampler. BS1 was taken from 120 – 140 cm and BS2 from 54 - 60 cm depth. The sample sites are located at Mosel River (km 211, km 183), Germany. SS was taken from the surface sediments of Mosel River (km 230) before a sluice. All samples were homogenized, stored in the dark at 4° C prior to freeze drying and ground < 2 mm with a ball mill (Fritsch).

Sample treatment was done according to Claus et al. (2002) until fractionation of the PAH containing solution. Two samples of each single sample (10 g of each) were extracted in an ultrasonic bath with a 4:2 acetone/heptane (v/v) solution. Centrifucation (3500 rpm for 20 min) was used to obtain the extract and a tetra butyl ammonia sulfite solution to remove sulphur. The samples were then separated into five fractions with a solid phase alumina oxide and silica-gel filled column. The third fraction contained the PAHs and was eluted with hexane/ethylacetate (70/30, v/v), filled in a flask and refilled to 4 ml with a 90:10 iso-hexane/dichloromethane solution (v/v). An amount of 1.8 ml was used for fractionation with HPLC (Agilent 1100, Agilent Technologies, Böblingen). Two solvents for chromatographic separations were used: 90 % of solvent A: iso-hexane and 10 % of solvent B: dichloromethane. During fractionation the flow rate was kept constant at 5 ml min^{-1}. Chromatographic separation was achieved at 25° C using a VP 250/10 Nucleosil 100-5 NO_2 column (Macherey-Nagel, Düren, Germany). Seven fractions were collected beginning at 4-8.5 min (F1), going on with 8.5-11 min (F2), 11-14 min (F3), 14-19 min (F4), 19-22.5 min (F5), 22.5-33 min (F6), 33-42 min (F7). After fractionation samples were evaporated with a TurboVap II (Zymark, Berlin, Germany) under a nitrogen stream to about 1 ml, adjusted with n-heptane and refilled to 3.6 ml. For Ames test 0.6 ml of

each fraction were used and diluted in dimethylsulfoxide (DMSO). For GC-MS analyses 0.01 ml of each fraction were used and 2.4 ml of a PAH surrogate (with deuterated PAHs naphthalene d8, acenaphtylene d8, phenanthrene d10, fluoranthene d10, pyrene d10, benz(a)pyrene d12, benz(ghi)perylene d12) added. No further sample treatment was necessary.

A group of 50 PAHs were analysed with GC-MS according to Pies et al. (2008). Compounds of each fraction F1-F6 are listed in Table 9. However, no PAHs are occurring in F7 for BS2 and SS. Due to analytical constraints a quantification of the highly toxic acting dibenzopyrenes was not possible. Only the existence of compounds with the mass 302 could be detected.

6.2.2 Ames Test

The Ames fluctuation test was performed according to Reifferscheid et al. (2005) using the tester strains TA98 and TA100. Strain TA98 detects frameshift mutations in the hisD3052 gene, whereas the TA100 strain is specific for G→A transition in hisG46, but is capable of detecting G→T and G→C transversions as well (Cebula and Koch 1990). Prior to the assays, the bacterial strains were grown overnight in Oxoid broth no.2 with shaking at 37° C. The resulting cultures of TA98 and TA100 were then diluted to approximately 10^8 cells ml^{-1} [TA 98] and 2.5 x 10^7 cells ml^{-1} [TA 100]. Ampicillin (50 µg/ml) was included in the overnight culture to select for plasmid pKM101. Chemical substances and extracts were diluted in 100% DMSO and 10 µl aliquots of test chemicals, diluted to the appropriate concentration, were added to the test culture (0.5 ml). After preincubation with and without S9 mix (100 min at 37°C with shaking; in triplicate for each condition) the mixtures were diluted sixfold in histidine-deficient minimal medium containing the pH indicator dye bromocresol purple (50 µg/ml). 50-µl aliquots of this mixture were distributed into the wells of 384-well plates (48 wells per replicate). The plates were then incubated for revertant selection at 37° C without shaking for 48 h. Revertant growth was detected by color change of the wells from purple to yellow caused by pH shift of the nutrient broth. Color change was measured at 420 nm (E420) using a 384-well plate reader.

6.2.3 Metabolic activation

S9 mix was used for providing exogenous metabolic activation. S9 was from RCC-CCR (Rossdorf, Germany). For preparing S9, male rats were pretreated with a single injection of β-naphthoflavon/phenobarbital for enzyme induction, the livers were homogenized in 0.15 M KCl, and the 9000 x g supernatants reserved. For the mutagenicity assays, a cofactor solution was always freshly prepared according to Maron and Ames (1983), combined with the S9, and maintained on ice until used in the test. The rat liver S9 concentration in all assays was fixed at 1% in order to provide similar test conditions as far as possible.

6.2.4 Data analysis

The statistical evaluation of the test systems used revertant wells from three replicates. In the mutagenicity tests the number of positive (yellow) wells out of 48 wells per replicate and concentration was compared with the number of spontaneous revertant wells of the negative control. Test substances were considered positive in the Ames fluctuation test when they produced statistically significant concentration-related increases in the number of revertant wells. The results were evaluated by the nonparametric Chi^2-assay as recommended by Green et al. (1976) and Gatehouse (1978), which is appropriate for the evaluation of fluctuation test data. Effects at $p<0.05$ were considered to be statistically significant. The mutagenic potential of the sample extracts was expressed as revertants mg^{-1} of sample.

6.3 Results and discussion

6.3.1 Chemical characteristics

Analyses of BS1, BS2 and SS were time-shifted so that compounds of BS1 were at the beginning in other fractions than in BS2 and SS. Additionally, only a part of the whole PAH spectrum was analyzed for BS1 (Table 9 and Table 10). Two to three ring PAHs were in fraction one (F1) for SS and BS2 (and in F1a and F1b in BS1). Fraction 2 (F2) included four ring PAHs, fraction 3 (F3) comprised four to five ring PAHs, fraction 4 (F4) included four to five ring PAHs, fraction 5 (F5) contained five to

six ring PAHs and fraction 6 (F6) comprised six ring PAHs of the mass 302. Concentrations are listed in Table 9 and Table 10.

Soil and sediment characteristics

Grain sizes for BS1 and BS2 were classified as a mixture of sand and silt and for SS as a mixture of clay and silt. The sample of BS1 is located on the bank of Mosel river before the confluence of Saar and Mosel and was contaminated by mainly pyrogenic PAHs and a small amount of lubricating oils (Pies et al. 2007). The sample of BS2 is located on the bank of Mosel river after the confluence of Saar, and was contaminated by pyrogenic and petrogenic PAHs. Due to coal mining activities in the region this soil contained coal particles and coal derived particles (Pies et al. 2007; Yang et al. 2008b). The sample of SS is a sediment from Mosel river before the confluence of the Saar, gathered from the surface of the river bed. Total organic carbon (TOC) content ranged from 4 – 15% for the soils and is 4% for the sediment.
Concentrations of the Σ16 EPA PAHs and the sum of all analyzed PAHs are displayed in Table 9 and Table 10.

Table 9: **PAH distribution in six PAH fractions and the concentrations (in mg kg^{-1}) of the sample SS and BS 2**.

PAH	SS	BS2	PAH	SS	BS2
F1	**F1**	**F1**	**F3**	**F3**	**F3**
Nap	0.0	2.8	Cpenta(c,d)py +B(ghi)flu	0.9	0.0
2-MNap	0.1	7.6	B(a)ant	3.7	4.8
1-MNap	0.0	5.6	Chr+Tr	4.9	3.5
2,3-Dnap	0.0	3.7	3-MChr	0.5	
Any	0.0	0.0	2-MChr	0.5	1.0
1,2-Dnap	0.0	1.7	5-MChr	0.0	0.5
Ace	0.5	0.2	1-MChr	0.0	0.5
2,3,5-Tnap	0.1	2.8	**Sum of F3**	**10.5**	**10.3**
Fl	1.7	0.6	**F4**	**F4**	**F4**
9,10-DHAnt	0.0	0.1	B(b)flu	3.0	2.3
1-MFl	0.2	0.6	B(k)flu	1.6	2.3
Dibenzo	0.3	0.3	7,12-Db(a)ant	0.0	0.0
Phe	7.7	9.1	B(a)flu	0.3	0.5
Ant	1.5	4.0	B(e)py	1.5	1.2
3-Mphe	1.6	2.6	B(a)py	3.3	2.1
2-Mphe	0.3	3.0	Per	0.8	0.5
2-Mant	0.4	3.7	**Sum of F4**	**10.5**	**8.9**
1-Mant	0.9	3.5	**F5**	**F5**	**F5**
4H-Cyclopenta(def)phe	2.5	1.3	Indeno	1.3	1.2
9-Mphe	0.5	2.9	Dib(a,h)ant +Dib(a,c)ant	0.9	0.4
1-Mphe	0.6	2.1	B(g,h,i)per	2.0	1.0
9-Mant	0.0	0.2	Anth	1.3	0.4
3,6-Dphe	0.2	0.7	**Sum of F5**	**5.5**	**3.0**
1,7-Dphe	0.1	2.0	**F6**	**F6**	**F6**
Sum of F1	**19.2**	**60.9**	M 302	1.2	0.5
F2	**F2**	**F2**	M 302	0.9	0.1
Flu	10.1	8.6	M 302	0.5	0.5
Py	7.3	6.6	M 302	0.0	0.1
B(a)fl	4.4	2.8	**Sum of F6**	**2.6**	**1.2**
1-Mpy	0.6	1.1			
B(b)naph(2,1-d)thio	0.8	0.5	**Sum of 16EPA PAH**	**49.6**	**49.6**
Sum of F2	**23.1**	**19.6**	**Sum of all PAH's**	**71.5**	**103.9**

Table 10: PAH distribution in six PAH fractions and the concentrations (in mg kg^{-1}) of the sample BS1 (compounds in grey are not analyzed).

PAH	BS1		PAH	BS1
F1a	**F1a**		**F3**	**F3**
Nap	0.02		B(a)ant	4.2
2-MNap			Chr+Tr	4.8
1-MNap			3-MChr	
2,3-Dnap			2-MChr	
Any	0.06		5-MChr	
1,2-Dnap			1-MChr	
Ace	0.3		**Sum of F3**	**9.0**
2,3,5-Tnap			**F4**	**F4**
Fl	0.3		B(b)flu	4.1
9,10-DHAnt			B(k)flu	4.3
1-MFl			7,12-Db(a)ant	
Dibenzo			B(a)flu	
Sum of F1a	**0.67**		B(e)py	3.3
F1b	**F1b**		B(a)py	4.5
Phe	3.8		Per	1.1
Ant	0.9		**Sum of F4**	**17.3**
3-Mphe			**F5**	**F5**
2-Mphe			Indeno	3.2
2-Mant			Dib(a,h)ant +Dib(a,c)ant	1.0
1-Mant	n.d.		B(g,h,i)per	3.1
4H-Cyclopenta(def)phe	0.9		Anth	
9-Mphe			**Sum of F5**	**7.2**
1-Mphe			**F6**	**F6**
9-Mant			M 302	1.0
3,6-Dphe			M 302	0.8
1,7-Dphe			M 302	0.4
Sum of F1b	**5.6**		M 302	0.1
F2	**F2**		**Sum of F6**	**2.3**
Flu	8.5			
Py	6.6		**Sum of 16EPA PAH**	**49.7**
B(a)fl	1.3		**Sum of all PAH's**	**58.5**
1-Mpy				
B(b)naph(2,1-d)thio				
Cpenta(c,d)py +B(ghi)flu				
Sum of F2	**16.4**			

6.3.2 Genotoxicity test (AMES)

The tests were performed with and without metabolic activation (+S9 and –S9), whereas PAHs are known to be genotoxic with metabolic activation (Harvey and Geacintov 1988). The results of the AMES test with the tester strains TA98 and TA100 showed predominantly frame shift mutations in the hisD3052 gene (TA98) and to a lower extent base pair substitutions (TA100) (Table 11).

Table 11: Ames test with and without metabolic activation (+S9 and –S9) of the tester strain TA98 and TA100 of the studied samples. Results are expressed as revertant wells mg^{-1} sediment or soil equivalent.

+S9 (Rev mg^{-1})	TA98	BS1	BS2	SS	TA100	BS1	BS2	SS
F0		6.7	6.4	8.5		3.4	5	2.4
F1a/F1b		< 1/1.4	1.2	< 1		<1	-	<1
F2		1	2.3	1.6		1	1.8	<1
F3		3.2	3.4	4.3		1.8	1	1.7
F4		7.4	8.1	11.1		4.2	4.3	6.6
F5		6.4	3.7	4.2		2.7	1.6	<1 (0.9)
F6		2.6	6.6	6		2.4	1.1	<1 (0.9)
-S9 (Rev mg^{-1})								
F0		5.3	5.3	5.5			2.5	1.7
F1a/F1b		< 1	1.3	< 1				<1
F2		< 1	3.5	< 1			<1	<1
F3		1	4.8	3.2			<1	<1
F4		1.1	4.3	7.2			<1	1.2
F5		3.5	3	<1			1.6	<1
F6		1.2	3.5	1.8			<1	<1

In Figure 18 the mutagenic potential of F4 of a repeat determination with metabolic activation (+S9) in sample SS is displayed graphically for tester strain TA98. With increasing concentrations of the extract a linear increase of the revertants can be observed. The gradients of the graphs show the revertant wells per mg of sediment which are displayed in Table 11 for all fractions. These gradients are mean values of repeat determinations.

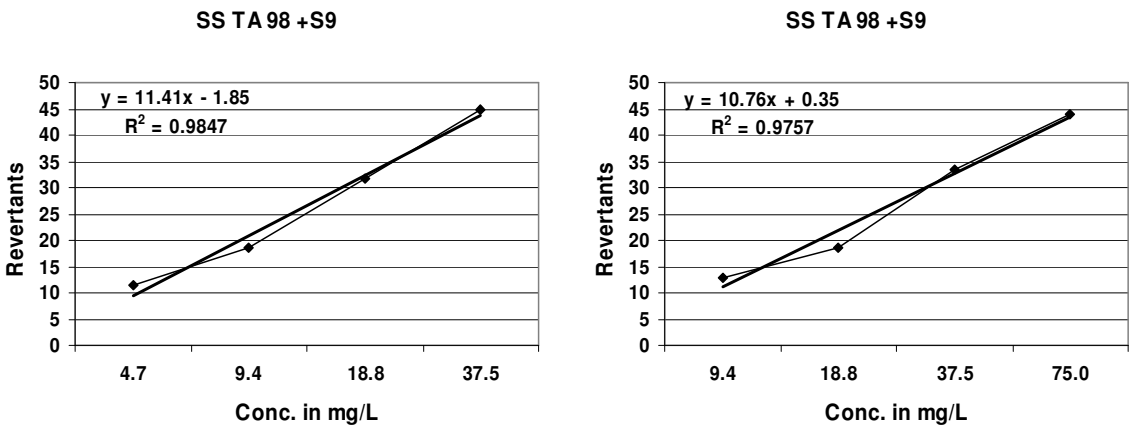

Figure 18: Gradients of the fraction F4 of SS with the tester strain TA98 and metabolic activation (+S9) of a repeat determination. The gradient correspond to revertant wells mg sediment^{-1}.

The following compounds were expected to contribute mainly to the genotoxic potential in the fractions:
fluoranthene in F2, cyclopenta(cd)pyrene and benz(a)anthracene in F3, benzo(b)fluoranthene, benzo(k)fluoranthene and benz(a)pyrene in F4, dibenz(ah)anthracene in F5, PAHs of the mass 302 in F6.
The soil BS1 with metabolic activation (+S9) showed the highest mutagenic potential in the fraction F4 containing benz(a)pyrene, benz(b)fluoranthene and benz(k)fluoranthene. The fractions F0 and F5 showed the next highest mutagenic potentials and the other fractions showed low to negligible potentials (Table 11, +S9). However, also without metabolic activation a mutagenic potential in strain TA98 could be observed in fraction F0, F5 and to minor significance in F4 and F6 (Table 11, –S9). The soil BS2 with metabolic activation (+S9) showed the highest mutagenic potential in the fraction F4 containing benz(a)pyrene, benz(b)fluoranthene and benz(k)fluoranthene, followed by F6 containing PAHs of the mass 302 and F0 (Table 11). As well as observed in BS1 a mutagenic potential without metabolic activation (-S9) in tester strain TA98 could be measured. In contrast to BS1 all fractions in BS2 showed reactions without metabolic activation (Table 11).

The sediment SS showed the highest mutagenic potential of the three studied samples. With +S9 the highest potential occurred in F4 containing benz(a)pyrene, benz(b)fluoranthene and benz(k)fluoranthene, followed by F0 and F6 containing PAHs of the mass 302. As well as in BS1 and BS2 a mutagenic potential could be observed without metabolic activation (–S9) in strain TA98. The potential was particularly high in F4 with 7.2 revertant wells mg^{-1}.

The mutagenic potential of the samples without metabolic activation could be explained either by other non identified substances not removed during preparation procedures or by an individual PAH mixture in the sample. GC-MS scans did not show any other peaks than PAH peaks. Therefore the individual PAH mixture of each fraction seems to be responsible for these results.

The fraction F4 of SS and BS1 containing benz(a)pyrene, benz(b)fluoranthene and benz(k)fluoranthene showed the highest mutagenic potentials. However, the potential in SS was higher than in BS1, although the benz(a)pyrene, benz(b)fluoranthene and benz(k)fluoranthene concentrations in SS were lower (Table 9, Table 10 and Table 11). The same could be observed in F0, where BS2 exhibited the highest concentrations. But here the high concentrations were related to the high content of two to three ring PAHs which are not genotoxic (Hermann 1981).

Nevertheless, without metabolic activation a mutagenic potential was evident in nearly all fractions of BS2 and SS in the tester strain TA98.

Despite low PAH concentrations the mutagenic potential of F6 in all samples was considerable. These fractions contained PAHs of the mass 302, including the high genotoxic dibenz(al)pyrene. In this study it is not known which mutagenic potential can be attributed to which isomers. But it is known, that dibenzo(al)pyrene is 10-100 times more toxic than benz(a)pyrene (Cavalieri et al. 1991).

Therefore, it is of great interest first to separate these isomers, in order to quantify them, and second to test and assess their toxic potential afterwards. Within this study only the assumption dibenz(al)pyrene being responsible for the mutagenic potential could be made. Concentrations and the proportion of the compounds to the genotoxicity were not known. However, the fraction containing compounds of the mass 302 showed half the genotoxic potential of the fraction containing

benz(a)pyrene, benz(b)fluoranthene and benz(k)fluoranthene and the concentrations are much lower.
In summary, the mutagenic potential (TA98 and TA100 with metabolic activation) of the samples were all in the same range meaning that no great differences could be identified. The tests without metabolic activation in the tester strain TA98 showed only small differences between BS2, SS and BS1 and nearly no differences in the tester strain TA100.

6.3.3 Conclusions

Concerning the soil-groundwater path for risk assessment PAHs showing mutagenic potentials are relative immobile due to their low water solubility. The mobile two to three ring PAHs did not show any mutagenic potential. Hence, the mutagenic PAHs are stored in soils and sediments and are only transported by particles. Nevertheless, animals such as worms are endangered due to their ingestion of soil particles. The study also showed that coal bearing soils at Mosel river do not exhibit a greater mutagenic potential than other soils or sediments without coal particles. The only difference in the PAH distribution pattern in these coal bearing soils are the concentrations of naphthalene and its alkylated derivatives and phenanthrene with its alkylated derivatives, and these compounds are not mutagenic (Hermann 1981). Hence, only the anthropogenic PAHs, identified as pyrogenic PAHs in (Pies et al. 2008), are responsible for the mutagenic potential in BS1, BS2 and SS.
Nevertheless, the concentrations of the sixteen EPA PAHs of all samples exceeded the German national guideline value Z2 of 30 mg kg^{-1} (LAGA 2004). If these soils or sediments would be dredged they have to be treated as hazardous waste.

6.3.4 Future Prospects

Within the scope of this study it was not possible to explain the mutagenic potentials of the PAHs without metabolic activation in the tester strain TA98. Additionally, due to analytical constraints PAH isomers of the mass 302 could not be separated and the mutagenic potential could not be attributed to a specific PAH in that group. To answer

these questions further research is required. Therefore, detailed tests have to be performed to elucidate the mutagenicity of specific PAH mixtures without their metabolization and the analytical method has to be improved to separate PAHs of mass 302.

7 Summary and Conclusions

PAHs are an ubiquitous class of contaminants and investigations of this study show large scale PAH contamination in floodplain soils collected from the Mosel and Saar River. PAH concentrations found in floodplain soils were up to 81 mg kg^{-1} for the sixteen EPA PAHs which is relatively high in comparison to other regions in the world. This value clearly exceeds the German LAGA Z2 guideline value of 30 mg kg^{-1}. Following this guideline those soils have to be treated as hazardous waste. In addition, most of the soils along the Mosel and Saar with high PAH concentrations also exhibit coal particles. However, the main problem of the contamination was the unknown PAH source.

To verify PAH sources a set of forensic methods could be used. The application of different source identification methods in the study area showed that combustion derived PAHs are dominant at sites before the confluence of the Mosel and Saar River, with an additional input of lubricating oils identified at the first sampling site of the Mosel River (refer to chapter 4). At sampling points at and after the confluence, a mixture of petrogenic and pyrogenic sources was found. The study also revealed that at sampling points at and after the confluence coal particles represent the main petrogenic input, with additional information provided from PAH analyses of coal samples collected from the Saarland as reference materials. It could be shown that in complex mixtures the analysis of parent PAHs is beneficial for the identification of pyrogenic sources, while the analysis of n-alkanes is essential to obtain detailed information about the petrogenic source (e.g. weathered lubricating oil). As could be shown in chapter 4, source identification of complex PAH mixtures requires more than one identification method to identify PAH source(s). Hence, a concept for source identification of bank soils was proposed: 1) collection of information about site history, 2) use of coal petrography if the samples are impacted by coal mining 3) selection and use of alkylated PAHs (i.e. methylnaphthalenes, methylphenanthrenes, methylanthracenes, methylfluoranthenes, methylpyrenes) with respect to distribution patterns and a calculation of PAH ratios, 4) interpretation of n-alkane measurements, 5) use of C_1-C_4 homologue series if data are available and 6) use of PCA. In case of

the coal impacted study area, additional coal petrography was essential for identifying coal and coal derived particles in the soils.

Further investigations could show that in addition to n-alkanes an extended PAH spectrum including alkylated PAHs is also essential for the identification of petrogenic inputs which otherwise would not have been possible using only the sixteen EPA PAHs (see chapter 5). Due to a shift from a pyrogenic to a petrogenic source, the PAH ratios are only helpful in characterizing samples (petrogenic vs. pyrogenic), if they are not derived from more than one potential source. However, using all methods described in chapter 4 and 5 is complex and expensive. In chapter 5 it could be shown that three relatively simple methods are sufficient for primary source identification of the investigated samples and to help direct further analytical steps. Therefore, we recommend the initial use of an extended PAH spectrum since it is cost effective with a simple analytical technique, before resorting to additional and expensive forensic investigations. Chapter 5 could demonstrate that using an extended, but easy to analyze, PAH spectrum can serve as a valuable first step toward source identification. The presence or absence of alkylated PAHs indicate that either a petrogenic or a non-petrogenic sample (e.g. coals for petrogenic samples) or a petrogenic/pyrogenic input has occurred. The methodology tested here simplifies the decision process about which forensic methods (see chapter 4) should be additionally used to obtain more detailed source identification.

However, complete analysis is only necessary if the exact sources should be identified. In most cases, the three methods applied in this study are sufficient.

Risk assessments of complex environmental samples is difficult due to the identification of the toxic components, the lack of available toxicity data and the limited knowledge of the behaviour of mutagenic substances in complex mixtures. Chapter 6 could show that coal bearing soils at the Mosel River do not exhibit a greater mutagenic potential than other soils or sediments without coal particles. The only difference in the PAH distribution pattern of these coal bearing soils are the concentrations of naphthalene and its alkylated derivatives and phenanthrene with its alkylated derivatives, and these compounds are not genotoxic. Hence, only the

anthropogenic PAHs, identified as pyrogenic PAHs, are responsible for the mutagenic potential in the investigated soils.
For risk assessments concerning the soil groundwater pathways in the Mosel area, it can be concluded that PAHs showing mutagenic potential are relative immobile due to their low water solubility. The mobile two to three ring PAHs did not show any mutagenic potential (see chapter 6). Hence, the mutagenic PAHs are sorbed to soils and sediments, and are only transported by particles. However, soil-dwelling organisms like worms are endangered due to their ingestion of soil particles.

The study clearly shows more than one method is required to accurately determine the source of contamination, in this case source of PAHs. The forensic investigations applied many different analytical techniques to identify the source of PAHs. The characterization of different kinds of crude oils, creosote and gasworks samples were the focus of these researchers. By means of these results source patterns could be identified. However, it is still difficult to identify PAH sources in environmental samples in which PAH mixtures are present and biodegradation can change the patterns observed. It would be beneficial to analyze the more resistant substances, but the costs would be high and most regulatory authorities who need the information about the sources would not able to afford it. In addition, these methods are still not applicable for routine analyses and currently only used for research purposes.

In chapter 6 the study shows the importance of dibenzopyrenes, especially dibenz(al)pyrene, which is 10-100 fold more mutagenic than benzo(a)pyrene. However, despite high quality analytical instruments and methods it is still difficult to analyze these compounds. For risk assessments of highly PAH contaminated sites these substances should be included. Further research in the field of simplifying analytical methods of very high molecular PAHs is needed. The advancement of these current methods would allow these substances to be included in routine analyses and risk assessments.

In chapter 4 an approach how to proceed in case of an unknown PAH source in river

bank soils was given, namely 1) collection of information about site history, 2) use of coal petrography if the samples are impacted by coal mining 3) selection and use of alkylated PAHs (i.e. methylnaphthalenes, methylphenanthrenes -anthracenes, methylfluoranthenes -pyrenes) with respect to distribution patterns and calculation of PAH ratios, 4) interpretation of n-alkane measurements, 5) use of C_1-C_4 homologue series if data are available and 6) use of PCA. This approach can be transferred to other source identification studies involving soils or sediments. However, depending on the alteration of the contamination further forensic methods have to be used which can be expensive. In that case only a small set of methods mentioned in chapter 5 should be applied. This approach does not necessarily determine the exact source of contamination, but provides to regulatory authorities a sufficient answer, and can be applied for most cases involving contaminated sites.

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Appendix

A) PAH concentrations at all sample sites

Table 12: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances in SP1 (C/C_{sum}).

SP1	0-20 cm		20-40 cm		40-60 cm		100-120 cm		120-140 cm		140-160 cm	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
Nap	0.29	0.64	0.32	0.34	0.32	0.36	0.54	0.94	0.90	0.76	0.36	0.47
2MNap	0.16	0.36	0.15	0.16	0.19	0.21	0.36	0.64	0.60	0.51	0.24	0.31
1MNap	0.12	0.27	0.09	0.10	0.13	0.15	0.19	0.33	0.27	0.23	0.13	0.17
Sum MNap	0.28	0.63	0.24	0.25	0.32	0.36	0.55	0.96	0.87	0.73	0.37	0.48
1,2DMNap	0.02	0.03	0.01	0.02	0.01	0.02	0.02	0.04	n.d.	n.d.	n.d.	n.d.
2,3DMNap	0.03	0.07	0.04	0.04	0.05	0.06	0.07	0.13	0.14	0.12	0.05	0.06
Sum DMNap	0.05	0.11	0.05	0.06	0.06	0.07	0.10	0.17	0.14	0.12	0.05	0.06
2,3,5TMNap	0.03	0.06	n.d.	n.d.	0.05	0.05	0.06	0.10	0.07	0.06	0.05	0.06
Any	0.32	0.72	0.73	0.78	0.55	0.62	0.54	0.95	1.12	0.95	0.60	0.77
Ace	0.11	0.25	0.19	0.21	0.22	0.24	0.30	0.53	0.45	0.38	0.16	0.21
Fl	0.27	0.59	0.46	0.49	0.44	0.49	0.43	0.76	0.53	0.45	0.34	0.44
1MFl	0.05	0.11	0.07	0.08	0.08	0.09	0.07	0.13	0.08	0.07	0.08	0.10
Dibenzo	0.10	0.22	0.15	0.16	0.14	0.16	0.15	0.27	0.25	0.21	0.17	0.22
Phe	2.05	4.56	3.59	3.85	4.11	4.65	3.34	5.85	7.12	6.04	4.10	5.25
1MPhe	0.22	0.49	0.43	0.46	0.44	0.50	0.37	0.65	0.83	0.70	0.56	0.72
2MPhe	0.34	0.76	0.57	0.61	0.60	0.67	0.55	0.97	1.10	0.93	0.69	0.89
3MPhe	0.28	0.62	0.48	0.52	0.48	0.54	0.35	0.61	0.87	0.74	0.40	0.51
9MPhe	0.25	0.56	0.47	0.51	0.51	0.58	0.43	0.75	0.80	0.68	0.51	0.66
Sum MPhe	1.09	2.43	1.95	2.09	2.03	2.29	1.69	2.97	3.60	3.05	2.17	2.78
3,6DMPhe	0.05	0.10	0.09	0.09	0.08	0.10	0.08	0.14	0.11	0.10	0.12	0.16
1,7DMPhe	0.38	0.84	0.83	0.89	0.85	0.96	0.63	1.10	0.61	0.52	0.34	0.43
Sum DMPhe	0.42	0.94	0.92	0.98	0.93	1.05	0.70	1.24	0.73	0.62	0.46	0.59
4H	0.62	1.38	1.21	1.29	1.16	1.31	0.74	1.30	1.23	1.05	0.98	1.26
Ant	0.69	1.53	1.35	1.45	1.17	1.33	0.82	1.44	1.22	1.03	0.92	1.18
1MAnt	0.34	0.76	0.55	0.63	0.54	0.61	0.40	0.70	0.78	0.66	0.57	0.73
2MAnt	0.11	0.25	0.23	0.24	0.21	0.23	0.17	0.30	0.27	0.23	0.25	0.32
9MAnt	0.02	0.05	0.04	0.05	0.04	0.04	0.03	0.06	0.06	0.05	0.05	0.07
Sum MAnt	0.47	1.05	0.82	0.93	0.78	0.88	0.60	1.06	1.11	0.94	0.87	1.12
Flu	5.80	12.88	11.43	12.27	10.80	12.19	7.90	13.85	17.53	14.86	10.85	13.90
Py	4.13	9.17	7.99	8.58	7.50	8.46	5.55	9.74	12.43	10.54	7.22	9.24
1MPy	0.19	0.43	0.28	0.30	0.26	0.30	0.22	0.38	0.34	0.29	0.36	0.46
B(a)Fl	1.07	2.38	2.07	2.22	1.85	2.09	1.16	2.03	1.71	1.45	1.75	2.24
B(b)naph(2,1-d)Th	0.74	1.64	1.17	1.25	1.08	1.22	0.83	1.46	1.71	1.45	1.40	1.80
Cpenta(cd)Py	1.19	2.63	2.26	2.42	2.17	2.45	1.21	2.11	2.93	2.49	1.43	1.83
B(a)Ant	1.51	3.34	3.18	3.41	2.90	3.28	2.04	3.58	4.12	3.49	2.77	3.55
Chr+Tri	1.65	3.66	3.39	3.63	2.99	3.37	2.16	3.79	5.28	4.48	2.97	3.81
1MChr	0.15	0.34	0.24	0.26	0.18	0.20	0.18	0.31	0.24	0.21	0.65	0.83
2MChr	0.31	0.69	0.41	0.45	0.25	0.28	0.35	0.62	1.38	1.17	1.20	1.54
3MChr	0.60	1.32	0.73	0.78	0.53	0.60	0.65	1.14	1.46	1.24	1.57	2.01
5MChr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum MChr	1.06	2.35	1.38	1.49	0.96	1.08	1.18	2.07	3.09	2.62	3.42	4.38
B(b)Flu	3.04	6.74	6.54	7.02	7.25	8.19	3.02	5.29	8.01	6.80	5.59	7.16
B(k)Flu	1.65	3.67	4.25	4.56	5.95	6.72	2.78	4.87	5.40	4.58	4.34	5.57
B(a)Flu	0.82	1.81	1.78	1.91	2.76	3.12	1.02	1.79	1.91	1.62	1.21	1.55
B(e)Py	2.08	4.63	4.80	5.15	4.09	4.62	2.66	4.67	6.71	5.69	2.48	3.17
B(a)Py	4.64	10.31	8.87	9.52	11.28	12.74	5.63	9.88	7.75	6.57	7.48	9.58
Per	1.08	2.40	1.73	1.86	1.72	1.95	1.12	1.97	2.04	1.73	1.50	1.92
Indeno	2.45	5.43	5.52	5.92	4.52	5.10	3.13	5.49	6.10	5.17	4.38	5.61
D(ah)Ant	0.61	1.35	1.21	1.30	0.99	1.11	0.74	1.29	1.28	1.08	1.00	1.28
B(ghi)Per	1.96	4.35	4.93	5.29	4.48	5.06	2.25	3.94	5.20	4.41	3.08	3.94
Anth	0.76	1.68	0.85	0.91	1.05	1.19	0.71	1.25	1.10	0.93	0.99	1.27
Sum 16EPA	**31.16**		**63.93**		**65.46**		**41.17**		**84.43**		**56.18**	
Sum all PAHs	**43.3**		**85.7**		**87.0**		**56.03**		**114.54**		**75.9**	

Table 13: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances in SP2 (C/C_{sum}).

SP2	0-20 cm		20-40 cm	
	M	C/Csum	M	C/Csum
Nap	0.11	0.42	0.10	0.54
2MNap	0.08	0.32	0.06	0.30
1MNap	0.04	0.17	0.03	0.18
Sum MNap	0.12	0.49	0.09	0.48
1,2DMNap	n.d.	n.d.	n.d.	n.d.
2,3DMNap	0.02	0.06	0.01	0.07
Sum DMNap	0.02	0.06	0.01	0.07
2,3,5TMNap	0.01	0.05	0.01	0.06
Any	0.16	0.65	0.13	0.72
Ace	0.06	0.23	0.04	0.22
Fl	0.11	0.43	0.07	0.39
1MFl	0.02	0.08	0.01	0.06
Dibenzo	0.04	0.17	0.03	0.15
Phe	1.04	4.13	0.92	4.90
1MPhe	0.13	0.53	0.12	0.62
2MPhe	0.17	0.70	0.17	0.91
3MPhe	0.15	0.60	0.13	0.72
9MPhe	0.16	0.63	0.12	0.65
Sum MPhe	0.62	2.46	0.54	2.90
3,6DMPhe	0.03	0.10	0.02	0.12
1,7DMPhe	0.24	0.95	0.23	1.24
Sum DMPhe	0.26	1.05	0.25	1.36
4H	0.35	1.39	0.29	1.53
Ant	0.35	1.39	0.20	1.08
1MAnt	0.21	0.83	0.17	0.89
2MAnt	0.07	0.29	0.06	0.33
9MAnt	0.01	0.04	0.01	0.05
Sum MAnt	0.29	1.16	0.24	1.27
Flu	3.01	12.01	2.34	12.52
Py	2.18	8.70	1.62	8.67
1MPy	0.07	0.29	0.05	0.29
B(a)Fl	0.52	2.06	0.35	1.89
B(b)naph(2,1-d)Th	0.30	1.19	0.22	1.20
Cpenta(c,d)Py	0.37	1.48	0.39	2.08
B(a)Ant	0.89	3.56	0.96	5.14
Chr+Tri	1.00	3.98	0.95	5.09
1MChr	0.02	0.09	0.02	0.13
2MChr	0.05	0.18	0.05	0.25
3MChr	0.18	0.72	0.18	0.97
5MChr	n.d.	n.d.	n.d.	n.d.

Continuation Table 13				
	0-20 cm		20-40 cm	
	M	C/Csum	M	C/Csum
Sum MChr	0.25	0.99	0.25	1.35
B(b)Flu	2.63	10.49	1.44	7.73
B(k)Flu	1.49	5.96	0.87	4.64
B(a)Flu	0.34	1.37	0.31	1.64
B(e)Py	2.04	8.12	1.02	5.44
B(a)Py	2.37	9.46	1.46	7.81
Per	0.54	2.16	0.35	1.88
Indeno	1.23	4.91	1.00	5.35
D(a,h)Ant	0.27	1.06	0.24	1.30
B(g,h,i)Per	1.31	5.22	0.96	5.14
Anth	0.21	0.84	0.23	1.22
Sum 16EPA PAHs	**18.21**		**13.30**	
Sum all PAHs	**26.53**		**19.83**	

Table 14: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances in SP3 (C/C_{sum}).

SP3	0-20 cm		20-40 cm		40-60 cm		60-80 cm		80-100 cm		100-120 cm		120-140 cm	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
Nap	3.03	5.93	3.80	7.21	3.92	6.33	7.24	5.06	8.22	5.74	7.48	6.35	9.57	4.78
2MNap	2.64	5.18	5.05	9.59	3.37	5.44	7.21	5.04	6.91	4.83	5.90	5.02	8.03	4.00
1MNap	1.71	3.35	3.01	5.71	2.41	3.89	4.39	3.06	4.39	3.07	4.39	3.73	6.56	3.27
Sum MNap	4.36	8.54	8.06	15.30	5.78	9.33	11.60	8.10	11.31	7.89	10.29	8.75	14.59	7.28
1,2DMNap	0.24	0.47	0.38	0.72	0.37	0.60	0.65	0.46	0.74	0.52	0.67	0.57	1.06	0.53
2,3DMNap	0.65	1.27	1.05	1.99	0.99	1.59	1.87	1.31	1.88	1.31	1.88	1.60	2.95	1.47
Sum DMNap	0.89	1.74	1.43	2.71	1.36	2.19	2.53	1.77	2.62	1.83	2.56	2.17	4.02	2.00
2,3,5TMNap	0.34	0.66	0.49	0.92	0.53	0.86	1.11	0.77	1.14	0.80	1.12	0.95	2.01	1.00
Any	0.23	0.45	0.25	0.48	0.29	0.47	0.64	0.44	0.78	0.54	0.54	0.46	0.83	0.41
Ace	0.14	0.27	0.12	0.22	0.13	0.20	0.42	0.29	0.46	0.32	0.44	0.37	0.54	0.27
Fl	0.22	0.43	0.16	0.31	0.22	0.36	0.72	0.50	0.88	0.62	0.65	0.56	1.23	0.61
1MFl	0.11	0.22	0.13	0.24	0.17	0.28	0.40	0.28	0.49	0.34	0.44	0.37	0.78	0.39
Dibenzo	0.11	0.22	0.08	0.15	0.13	0.20	0.27	0.19	0.34	0.24	0.30	0.26	0.50	0.25
Phe	3.36	6.58	3.59	6.82	3.78	6.10	8.17	5.70	9.49	6.63	7.29	6.19	14.48	7.22
1MPhe	0.67	1.31	0.49	0.94	0.82	1.32	1.55	1.08	1.87	1.30	1.47	1.25	2.70	1.34
2MPhe	0.56	1.10	0.43	0.81	0.77	1.24	1.37	0.95	1.73	1.21	1.42	1.20	2.63	1.31
3MPhe	0.53	1.05	n.d.	n.d.	0.68	1.10	1.35	0.94	1.49	1.04	1.23	1.05	1.85	0.92
9MPhe	0.69	1.35	0.47	0.89	0.96	1.55	1.76	1.23	1.93	1.34	1.63	1.39	2.85	1.42
Sum MPhe	2.45	4.80	1.39	2.64	3.23	5.21	6.02	4.20	7.01	4.89	5.76	4.89	10.03	5.00
3,6DMPhe	0.11	0.22	n.d.	n.d.	0.14	0.23	0.26	0.18	0.31	0.22	0.20	0.17	0.16	0.08
1,7DMPhe	1.35	2.65	0.35	0.67	1.15	1.86	3.18	2.22	2.64	1.84	2.72	2.31	5.35	2.67
Sum DMPhe	1.46	2.86	0.35	0.67	1.30	2.09	3.44	2.40	2.95	2.06	2.93	2.49	5.51	2.75
4H	0.72	1.41	0.24	0.45	0.62	1.00	1.96	1.37	1.76	1.23	1.35	1.15	2.79	1.39
Ant	0.82	1.60	0.62	1.17	1.04	1.68	3.50	2.44	4.10	2.86	2.59	2.20	5.76	2.87
1MAnt	0.84	1.64	0.42	0.79	0.60	0.96	0.97	0.68	2.35	1.64	1.69	1.44	1.98	0.99
2MAnt	0.31	0.61	0.31	0.59	0.48	0.78	1.00	0.70	1.23	0.86	0.87	0.74	1.30	0.65
9MAnt	0.07	0.13	n.d.	n.d.	0.09	0.15	n.d.	n.d.	0.21	0.14	0.18	0.16	0.32	0.16
Sum MAnt	1.22	2.39	0.73	1.38	1.17	1.89	1.97	1.38	3.79	2.64	2.75	2.34	3.60	1.80
Flu	5.25	10.28	6.41	12.17	6.05	9.77	12.82	8.95	15.93	11.12	12.11	10.29	26.41	13.18
Py	3.84	7.53	4.76	9.03	4.63	7.47	9.70	6.77	12.01	8.38	9.64	8.19	19.76	9.86
1MPy	0.26	0.50	0.11	0.22	0.35	0.56	0.42	0.29	0.71	0.49	0.56	0.47	1.04	0.52
B(a)Fl	1.00	1.96	0.34	0.65	1.28	2.07	1.95	1.36	2.83	1.97	2.96	2.52	4.23	2.11
B(b)naph(2,1-d)Th	0.63	1.24	0.11	0.21	0.49	0.80	0.55	0.38	0.91	0.63	0.77	0.65	1.23	0.61

Continuation Table 14														
	0-20 cm		20-40 cm		40-60 cm		60-80 cm		80-100 cm		100-120 cm		120-140 cm	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
Cpenta(c,d)Py	1.08	2.12	0.45	0.85	1.57	2.53	1.53	1.07	3.51	2.45	1.88	1.60	3.45	1.72
B(a)Ant	1.96	3.85	1.14	2.16	2.59	4.18	2.99	2.09	4.23	2.95	3.04	2.58	5.67	2.83
Chr+Tri	1.83	3.59	1.44	2.37	2.21	3.58	3.47	2.42	3.72	2.60	3.13	2.66	5.43	2.71
1MChr	0.53	1.03	0.05	0.09	0.15	0.25	0.17	0.12	0.32	0.22	0.30	0.25	0.49	0.25
2MChr	0.17	0.33	0.07	0.14	0.23	0.37	0.25	0.17	0.52	0.36	0.58	0.50	0.59	0.29
3MChr	0.87	1.71	0.39	0.73	0.66	1.07	0.80	0.56	1.12	0.78	0.86	0.73	1.62	0.81
5MChr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum MChr	1.57	3.08	0.51	0.97	1.04	1.69	1.21	0.85	1.96	1.37	1.74	1.48	2.70	1.35
B(b)Flu	2.26	4.42	3.00	5.69	2.88	4.65	5.46	3.81	5.47	3.82	4.84	4.11	8.26	4.12
B(k)Flu	1.33	2.61	1.70	3.22	1.73	2.80	3.87	2.70	3.86	2.69	3.25	2.76	4.05	2.02
B(a)Flu	0.59	1.15	0.59	1.11	0.74	1.20	1.60	1.12	1.86	1.30	1.39	1.18	2.24	1.12
B(e)Py	1.50	2.95	2.34	4.45	1.95	3.15	4.04	2.82	3.88	2.71	3.44	2.92	6.49	3.24
B(a)Py	2.57	5.03	2.62	4.97	3.29	5.31	6.22	4.35	11.37	7.94	10.58	8.99	13.32	6.64
Per	0.58	1.15	0.63	1.19	0.73	1.18	1.38	0.96	1.75	1.22	1.34	1.14	2.35	1.17
Indeno	1.58	3.09	1.66	3.14	2.03	3.27	3.26	2.28	4.32	3.02	3.29	2.80	6.12	3.05
D(a,h)Ant	0.38	0.74	0.36	0.68	0.50	0.81	0.84	0.59	1.11	0.78	0.88	0.75	1.52	0.76
B(g,h,i)Per	1.54	3.02	1.63	3.10	2.00	3.23	2.97	2.07	4.01	2.80	2.84	2.41	4.83	2.41
Anth	0.52	1.01	0.39	0.74	0.67	1.09	0.87	0.61	1.65	1.15	1.14	0.97	1.88	0.94
Sum 16EPA PAHs	**30.33**		**33.24**		**37.30**		**72.30**		**89.97**		**72.57**		**127.7**	
Sum all PAHs	**50.03**		**52.66**		**61.93**		**116.5**		**143.2**		**117.6**		**197.2**	

Table 15: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances in SP4 (C/C_{sum}).

SP4	40-54 cm		54-60 cm		60-80 cm	
	M	C/Csum	M	C/Csum	M	C/Csum
Nap	7.04	4.26	13.74	8.32	3.37	6.22
2MNap	6.49	3.93	15.18	9.18	3.00	5.53
1MNap	4.69	2.84	12.62	7.63	2.19	4.04
Sum MNap	11.18	6.76	27.79	16.81	5.19	9.57
1,2DMNap	0.78	0.47	1.62	0.98	0.34	0.63
2,3DMNap	2.10	1.27	4.50	2.72	0.98	1.80
Sum DMNap	2.88	1.75	6.12	3.70	1.32	2.43
2,3,5TMNap	1.41	0.85	2.63	1.59	0.52	0.95
Any	0.41	0.25	0.42	0.26	0.29	0.53
Ace	0.18	0.11	0.23	0.14	0.11	0.21
Fl	0.37	0.22	0.63	0.38	0.19	0.35
1MFl	0.31	0.19	0.84	0.51	0.13	0.23
Dibenzo	0.19	0.12	0.31	0.19	0.10	0.19
Phe	5.41	3.27	12.82	7.76	3.42	6.31
1MPhe	1.58	0.95	2.81	1.70	0.76	1.40
2MPhe	1.34	0.81	2.26	1.37	0.64	1.19
3MPhe	1.04	0.63	2.01	1.22	n.d.	n.d.
9MPhe	1.62	0.98	1.70	1.03	0.46	0.85
Sum MPhe	5.58	3.37	8.79	5.32	1.86	3.43
3,6DMPhe	0.26	0.16	0.27	0.16	n.d.	n.d.
1,7DMPhe	1.68	1.02	1.91	1.16	0.53	0.99
Sum DMPhe	1.94	1.17	2.18	1.32	0.53	0.99
4H	0.98	0.59	2.08	1.26	0.38	0.71
Ant	1.72	1.04	3.03	1.84	0.91	1.68
1MAnt	1.48	0.89	2.74	1.66	0.56	1.04
2MAnt	0.94	0.57	1.82	1.10	0.45	0.83
9MAnt	0.17	0.10	0.09	0.05	n.d.	n.d.
Sum MAnt	2.59	1.57	4.65	2.81	1.01	1.86
Flu	8.66	5.24	14.32	8.66	5.98	11.03
Py	6.48	3.92	13.17	7.97	4.46	8.22
1MPy	0.63	0.38	0.65	0.39	0.25	0.45
B(a)Fl	1.50	0.91	1.81	1.09	0.70	1.30
B(b)naph(2,1-d)Th	0.88	0.53	0.52	0.31	0.30	0.56
Cpenta(c,d)Py	2.10	1.27	1.37	0.83	0.90	1.66
B(a)Ant	3.20	1.93	5.16	3.12	2.24	4.13
Chr+Tri	2.92	1.76	5.67	3.43	2.37	4.30
1MChr	0.30	0.18	0.37	0.22	0.13	0.23
2MChr	0.44	0.27	0.60	0.36	0.20	0.37
3MChr	0.98	0.59	0.94	0.57	0.58	1.08
5MChr	n.d.	n.d.	0.22	0.13	0.02	0.03

Continuation Table 15						
	40-54 cm		54-60 cm		60-80 cm	
	M	C/Csum	M	C/Csum	M	C/Csum
Sum MChr	1.73	1.05	2.13	1.29	0.93	1.72
B(b)Flu	4.05	2.45	5.02	3.04	2.71	4.99
B(k)Flu	2.53	1.53	3.16	1.91	1.56	2.87
B(a)Flu	1.10	0.67	1.13	0.68	0.66	1.23
B(e)Py	2.65	1.61	3.82	2.31	2.10	3.87
B(a)Py	4.74	2.87	5.36	3.24	2.78	5.12
Per	1.11	0.67	1.12	0.68	0.74	1.37
Indeno	2.72	1.64	2.91	1.76	1.98	3.65
D(a,h)Ant	0.67	0.40	0.85	0.51	0.50	0.92
B(g,h,i)Per	2.56	1.55	2.92	1.77	1.78	3.28
Anth	1.00	0.61	0.85	0.51	0.50	0.93
Sum 16EPA PAHs	**53.65**		**89.40**		**34.64**	
Sum all PAHs	**95.46**		**158.44**		**52.80**	

Table 16: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances in SP5 (C/C_{sum}).

SP5	0-20 cm		20-40 cm		40-60 cm	
	M	C/Csum	M	C/Csum	M	C/Csum
Nap	0.81	4.31	1.05	4.50	1.04	4.41
2MNap	0.82	4.36	0.86	3.69	0.87	3.69
1MNap	0.54	2.88	0.63	2.71	0.64	2.73
Sum MNap	1.36	7.24	1.49	6.40	1.51	6.43
1,2DMNap	0.13	0.71	0.11	0.47	0.11	0.48
2,3DMNap	0.25	1.31	0.26	1.14	0.30	1.27
Sum DMNap	0.38	2.03	0.37	1.61	0.41	1.75
2,3,5TMNap	0.14	0.74	0.23	0.98	0.24	1.01
Any	0.09	0.46	0.10	0.42	0.11	0.45
Ace	0.06	0.33	0.03	0.15	0.05	0.20
Fl	0.07	0.38	0.05	0.23	0.06	0.27
1MFl	0.04	0.21	0.06	0.24	0.06	0.25
Dibenzo	0.04	0.19	0.04	0.17	0.04	0.16
Phe	0.91	4.80	1.06	4.55	1.05	4.48
1MPhe	0.23	1.21	0.26	1.11	0.28	1.19
2MPhe	0.20	1.06	0.21	0.92	0.25	1.07
3MPhe	n.d.	n.d.	0.18	0.79	0.22	0.94
9MPhe	0.46	2.46	0.29	1.25	0.31	1.33
Sum MPhe	0.89	4.72	0.95	4.07	1.07	4.53
3,6DMPhe	n.d.	n.d.	0.04	0.18	0.04	0.18
1,7DMPhe	0.19	0.99	0.76	3.27	0.82	3.49
Sum DMPhe	0.19	0.99	0.80	3.45	0.87	3.67
4H	0.15	0.82	0.20	0.86	0.23	0.99
Ant	0.26	1.38	0.30	1.27	0.32	1.38
1MAnt	0.17	0.92	0.40	1.70	0.43	1.84
2MAnt	0.15	0.79	0.08	0.36	0.11	0.45
9MAnt	n.d.	n.d.	n.d.	n.d.	0.02	0.09
Sum MAnt	0.32	1.71	0.48	2.06	0.56	2.38
Flu	1.72	9.11	1.90	8.16	2.00	8.48
Py	1.33	7.05	1.65	7.10	1.65	7.01
1MPy	0.12	0.63	0.08	0.35	0.09	0.36
B(a)Fl	0.28	1.47	0.94	4.04	0.98	4.17
B(b)naph(2,1-d)Th	0.17	0.89	0.12	0.54	0.13	0.57
Cpenta(c,d)Py	0.43	2.29	0.17	0.71	0.20	0.84
B(a)Ant	0.95	5.04	0.39	1.67	0.43	1.85
Chr+Tri	1.07	5.39	0.66	2.25	0.56	2.36
1MChr	0.06	0.30	0.10	0.45	0.10	0.41
2MChr	0.10	0.55	0.19	0.81	0.19	0.81
3MChr	0.45	2.38	0.18	0.76	0.17	0.72
5MChr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Continuation Table 16						
	0-20 cm		20-40 cm		40-60 cm	
	M	C/Csum	M	C/Csum	M	C/Csum
Sum MChr	0.61	3.24	0.47	2.02	0.46	1.94
B(b)Flu	1.09	5.78	1.07	4.59	1.11	4.70
B(k)Flu	0.55	2.94	0.88	3.80	0.92	3.89
B(a)Flu	0.27	1.41	0.40	1.74	0.40	1.70
B(e)Py	0.80	4.27	0.76	3.27	0.76	3.22
B(a)Py	1.05	5.59	2.02	8.69	1.85	7.83
Per	0.35	1.87	0.34	1.46	0.29	1.24
Indeno	0.73	3.88	0.98	4.23	0.85	3.62
D(a,h)Ant	0.19	1.03	0.25	1.07	0.24	1.00
B(g,h,i)Per	0.66	3.50	1.03	4.41	1.01	4.27
Anth	0.19	1.01	0.45	1.96	0.37	1.59
Sum 16EPA PAHs	**11.55**		**13.41**		**13.24**	
Sum all PAHs	**18.73**		**22.13**		**22.17**	

B) PAH concentrations of sites of chapter 5 and coals

Table 17: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances (C/C_{sum}) of sites of chapter 5.

	TF		TIF		D		GW 1		GW 2		CT		AT	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
Nap	6.3	16.8	38.5	3.7	0.0	2.9	255.7	25.0	336.9	20.8	185.7	0.1	389.1	6.4
2MNap	9.1	24.4	42.1	4.1	0.0	2.5	56.1	5.5	70.0	4.3	402.7	0.2	220.0	3.6
1MNap	6.2	16.7	40.6	3.9	0.0	1.4	33.6	3.3	37.3	2.3			92.9	1.5
Sum 1MNap	15.3	41.2	82.7	8.0	0.0	3.9	89.7	8.8	107.2	6.6	402.7	0.2	313.0	5.1
1,2DMNap	1.2	3.3	2.4	0.2	0.0	1.7	3.3	0.3	n.d.	n.d.	384.8	0.2	9.4	0.2
2,3DMNap	2.8	7.6	6.2	0.6	0.0	0.1	5.6	0.6	6.1	0.4	373.5	0.2	23.3	0.4
Sum 2MNap	4.1	10.9	8.6	0.8	0.0	1.9	8.9	0.9	6.1	0.4	758.4	0.4	32.6	0.5
2,3,5TMNap	2.8	7.6	1.8	0.2	n.d.	n.d.	n.d.	n.d.	2.2	0.1	232.2	0.1	7.5	0.1
Any	0.0	0.1	0.7	0.1	0.0	0.3	37.0	3.6	50.9	3.1	94.2	0.1	9.0	0.1
Ace	0.3	0.7	84.8	8.2	0.0	0.4	10.8	1.1	14.9	0.9	7955	4.3	104.5	1.7
Fl	0.9	2.3	91.9	8.8	0.0	0.4	39.7	3.9	50.4	3.1	8794	4.7	533.7	8.8
1MFl	1.4	3.9	3.9	0.4	0.0	0.8	2.8	0.3	2.9	0.2	796.2	0.4	28.8	0.5
Dibenzo	1.5	4.0	26.9	2.6	0.0	0.4	5.3	0.5	11.4	0.7	2845	1.5	182.6	3.0
Phe	0.9	2.3	238.1	22.9	0.0	3.7	127.9	12.5	207.9	12.8	36443	19.5	1602.6	26.3
1MPhe	0.6	1.7	8.4	0.8	0.0	1.3	6.5	0.6	12.3	0.8	3394	1.8	59.1	1.0
2MPhe	0.7	1.8	18.0	1.7	0.0	0.9	10.7	1.0	13.2	0.8	6202	3.3	159.1	2.6
3MPhe	0.5	1.2	17.5	1.7	0.0	0.7	8.6	0.8	n.d.	n.d.	2816	1.5	142.4	2.3
9MPhe	n.d.	n.d.	10.5	1.0	n.d.	n.d.	6.0	0.6	46.1	2.8	1534	0.8	129.8	2.1
Sum 1MPhe	1.7	4.7	54.4	5.2	0.0	3.0	31.8	3.1	71.7	4.4	13947	7.5	490.4	8.1
3,6DMPhe	0.2	0.4	1.5	0.1	0.0	2.4	1.0	0.1	n.d.	n.d.	708.8	0.4	18.3	0.3
1,7DMPhe	0.3	0.8	7.9	0.8	0.1	7.2	8.2	0.8	n.d.	n.d.	822.6	0.4	27.8	0.5
Sum 2MPhe	0.5	1.2	9.5	0.9	0.1	9.7	9.2	0.9	n.d.	n.d.	1531	0.8	46.2	0.8
4H	n.d.	n.d.	34.4	3.3	0.0	1.9	20.8	2.0	23.1	1.4	8284	4.4	77.0	1.3
Ant	n.d.	n.d.	16.5	1.6	0.0	1.3	26.2	2.6	39.2	2.4	7870	4.2	249.1	4.1
1MAnt	1.3	3.6	14.3	1.4	0.0	1.5	13.2	1.3	7.9	0.5	2639	1.4	81.1	1.3
2MAnt	n.d.	n.d.	2.2	0.2	0.0	0.7	5.9	0.6	7.6	0.5	1519	0.8	68.1	1.1
9MAnt	n.d.	n.d.	0.8	0.1	0.0	0.9	n.d.	n.d.	n.d.	n.d.	307.2	0.2	0.0	0.0
Sum 1MAnt	1.3	3.6	17.2	1.7	0.0	3.1	19.1	1.9	15.5	1.0	4465	2.4	149.2	2.5
Flu	0.1	0.2	170.5	16.4	0.1	7.5	80.9	7.9	151.3	9.3	45203	24.2	779.4	12.8
Py	0.1	0.2	87.8	8.5	0.1	11.4	62.7	6.1	111.9	6.9	24626	13.2	172.3	2.8
1MPy	n.d.	n.d.	1.6	0.2	0.0	3.6	2.3	0.2	4.4	0.3	619.2	0.3	6.7	0.1
B(a)Fl	n.d.	n.d.	7.5	0.7	0.1	2.2	13.4	1.3	15.6	1.0	4585	2.5	147.5	2.4
B(b)naph(2,1-d)Th	0.0	0.1	7.5	0.7	0.0	1.1	2.5	0.2	6.1	0.4	1718	0.9	84.4	1.4
Cpenta(c,d)Py	n.d.	n.d.	0.2	0.0	n.d.	n.d.	5.5	0.5	15.5	1.0	107.9	0.06	1.5	0.0
B(a)Ant	0.0	0.0	9.1	0.9	0.0	2.3	12.4	1.2	48.1	3.0	4962	2.7	187.2	3.1
Chr+Tri	0.0	0.0	9.0	0.9	0.0	3.2	9.7	0.9	n.d.	n.d.	2538	1.4	163.6	2.7

	TF		TIF		D		GW 1		GW 2		CT		AT	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
1MChr	n.d.	n.d.	0.7	0.1	n.d.	n.n	1.4	0.1	2.7	0.2	116.9	0.1	11.0	0.2
2MChr	n.d.	n.d.	1.7	0.2	0.0	0.9	2.4	0.2	3.1	0.2	242.4	0.1	29.4	0.5
3MChr	n.d.	n.d.	2.3	0.2	0.0	2.4	8.6	0.8	32.6	2.0	1193	0.6		0.0
Sum 1MChr	n.d.	n.d.	4.7	0.5	0.0	3.3	12.5	1.2	38.5	2.4	1553	0.8	40.3	0.7
B(b)Flu	0.0	0.1	5.8	0.6	0.0	4.7	12.3	1.2	44.0	2.7	1637	0.9	54.0	0.9
B(k)Flu	n.d.	n.d.	4.2	0.4	0.0	1.7	9.5	0.9	22.9	1.4	948.9	0.5	39.7	0.7
B(a)Flu	n.d.	n.d.	1.7	0.2	n.d.	n.d.	5.4	0.5	13.3	0.8	376.1	0.2	13.7	0.2
B(e)Py	0.0	0.1	3.1	0.3	0.0	3.8	14.4	1.4	33.1	2.0	885.2	0.5	18.7	0.3
B(a)Py	0.0	0.1	9.1	0.9	0.1	7.6	44.4	4.4	47.1	2.9	1065	0.6	1.6	0.0
Per	n.d.	n.d.	1.2	0.1	0.0	4.1	6.2	0.6	19.5	1.2	428.344	0.2	1.2	0.0
Indeno	0.0	0.0	1.2	0.1	0.0	2.7	14.8	1.4	29.5	1.8	288.9	0.2	0.4	0.0
D(a,h)Ant	0.0	0.0	0.4	0.0	n.d.	n.d.	2.7	0.3	7.2	0.4	108.5	0.06	1.3	0.0
B(g,h,i)Per	n.d.	n.d.	1.2	0.1	0.0	4.1	13.5	1.3	26.8	1.7	198.7	0.1	3.0	0.0
Anth	n.d.	n.d.	0.5	0.0	n.d.	n.d.	4.3	0.4	8.4	0.5	49	0.03	0.4	0.0
Sum 16EPA PAHs	**8.5**		**768.8**		**0.5**		**760.1**		**1188.9**		**142918**		**4290.4**	
Sum all PAHs	**37.3**		**1036.4**		**1.1**		**1014**		**1582.9**		**186738**		**5932.8**	

Table 18: PAH concentrations in mg kg^{-1} (M = Mean) and the proportion of the single substance to the sum of all substances (C/C_{sum}) of coals.

	MVBC		HVBC1		HVBC2		HVBC3		Ant		HC1		HC2		HC3		FC	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
Nap	16.9	24.8	40.2	24.2	0.1	0.4	3.3	6.4	0.1	11.9	7.7	6.1	1.1	1.7	15.8	18.9	24.8	19.1
2MNap	15.7	23.1	39.9	24.1	0.1	0.4	5.3	10.3	0.1	7.1	23.8	18.6	4.0	6.5	19.3	23.1	28.0	21.6
1MNap	10.6	15.6	27.5	16.6	0.1	0.6	4.2	8.2	n.d.		20.3	15.9	5.9	9.5	12.6	15.0	19.9	15.3
Sum MNap	26.3	38.7	67.4	40.6	0.2	1.0	9.5	18.5	0.1	7.1	44.1	34.5	9.9	15.9	31.9	38.2	47.9	36.9
1,2DMNap	1.0	1.5	3.5	2.1	0.3	1.0	1.6	3.1	n.d.		2.9	2.3	1.8	2.9	2.5	3.0	2.8	2.1
2,3DMNap	3.8	5.6	8.8	5.3	0.3	1.1	2.6	5.1	0.0	0.9	9.2	7.2	3.5	5.6	3.9	4.7	5.3	4.1
Sum DMNap	4.8	7.1	12.3	7.4	0.5	2.1	4.2	8.2	0.0	0.9	12.1	9.5	5.3	8.5	6.4	7.7	8.0	6.2
2,3,5TMNap	2.3	3.4	5.8	3.5	0.7	2.8	2.1	4.1	n.d.		5.2	4.1	2.0	3.2	1.9	2.2	1.9	1.5
Any	n.d.	n.d.	n.d.	n.d.	0.0	0.0	n.d.		n.d.		n.d.	n.d.	0.0	0.0	0.0	0.1	0.1	0.0
Ace	0.1	0.1	n.d.	n.d.	0.1	0.3	0.3	0.6	n.d.		0.2	0.1	0.3	0.4	0.1	0.1	0.1	0.1
Fl	0.1	0.2	0.2	0.1	0.1	0.5	0.8	1.6	0.0	2.6	0.6	0.5	0.6	1.0	0.8	0.9	1.4	1.1
1MFl	0.3	0.4	0.8	0.5	1.2	4.6	1.1	2.1	n.d.		1.5	1.2	1.5	2.4	1.4	1.6	2.0	1.5
Dibenzo	0.1	0.2	0.2	0.1	0.1	0.4	0.2	0.4	0.0	2.5	0.3	0.3	0.3	0.5	0.1	0.2	0.4	0.3
Phe	3.2	4.7	6.7	4.1	0.8	3.3	2.7	5.2	0.1	7.0	9.4	7.4	3.0	4.9	2.7	3.2	5.1	3.9
1MPhe	1.6	2.4	3.9	2.4	1.0	4.1	3.3	6.4	0.0	1.3	4.2	3.3	4.9	7.9	3.4	4.1	4.7	3.6
2MPhe	1.3	2.0	3.2	1.9	1.2	4.6	1.5	2.9	0.0	2.5	3.2	2.5	2.7	4.3	2.5	3.0	3.9	3.0
3MPhe	1.0	1.5	2.2	1.3	1.0	3.8	1.3	2.5	0.0	1.6	2.5	2.0	2.3	3.8	2.0	2.4	3.1	2.4
9MPhe	1.5	2.3	4.1	2.5	1.3	4.9	3.8	7.4	0.0	1.6	5.0	4.0	7.8	12.6	2.9	3.5	5.1	3.9
Sum MPhe	5.5	8.1	13.5	8.1	4.4	17.5	9.9	19.2	0.1	7.0	14.9	11.7	17.8	28.6	10.8	13.0	16.7	12.9
3,6DMPhe	1.1	1.7	5.8	3.5	1.7	6.5	0.5	0.9	0.0	0.3	4.3	3.4	0.6	1.0	0.5	0.5	0.6	0.5
1,7DMPhe	0.2	0.3	0.5	0.3	0.2	0.7	1.5	2.9	n.d.		0.5	0.4	3.4	5.4	1.7	2.0	2.0	1.5
Sum DMPhe	1.4	2.0	6.4	3.8	1.8	7.2	2.0	3.8	0.0	0.3	4.9	3.8	4.0	6.4	2.1	2.5	2.6	2.0
4H	n.d.	n.d.	n.d.	n.d.	0.1	0.6	0.3	0.6	0.0	0.5	0.3	0.3	0.2	0.4	0.1	0.2	0.3	0.2
Ant	0.8	1.2	0.4	0.2	0.4	1.5	0.6	1.2	0.0	0.3	1.9	1.5	1.1	1.8	0.7	0.8	1.1	0.8
1MAnt	1.8	2.6	4.2	2.5	1.6	6.4	1.8	3.5	0.0	1.1	5.0	3.9	2.3	3.8	1.4	1.7	2.4	1.9
2MAnt	0.7	1.0	0.6	0.4	1.6	6.4	0.8	1.6	n.d.	0.0	1.7	1.4	2.1	3.4	0.8	0.9	0.8	0.6
9MAnt	1.5	2.3	4.1	2.5	1.3	4.9	3.8	7.4	0.0	1.6	5.0	4.0	7.8	12.6	2.9	3.5	5.1	3.9
Sum MAnt	4.0	5.9	8.9	5.4	4.5	17.8	6.4	12.5	0.0	2.7	11.8	9.2	12.3	19.7	5.1	6.1	8.3	6.4
Flu	0.3	0.4	0.4	0.3	0.8	3.1	0.5	0.9	0.0	1.2	1.6	1.3	0.5	0.8	0.2	0.2	0.4	0.3
Py	0.4	0.5	0.6	0.4	1.0	3.9	0.8	1.5	0.0	2.4	2.4	1.9	0.6	1.0	0.3	0.4	0.7	0.5
1MPy	0.2	0.3	0.5	0.3	0.6	2.4	1.0	1.8	0.0	0.4	1.4	1.1	0.7	1.2	0.5	0.6	0.9	0.7
B(a)Fl	0.3	0.5	0.9	0.6	1.3	5.2	1.3	2.5	0.0	2.4	1.6	1.3	1.9	3.0	1.3	1.6	2.0	1.6
B(b)naph(2,1-d)Th	n.d.	n.d.	n.d.	n.d.	0.2	0.9	0.2	0.3	0.0	1.4	n.d.	n.d.	0.2	0.3	0.1	0.1	0.2	0.2
Cpenta(c,d)Py	n.d.	n.d.	n.d.	n.d.	0.2	0.9	0.1	0.1	0.0	0.2	n.d.	n.d.	0.3	0.4	0.1	0.1	0.2	0.2
B(a)Ant	0.2	0.3	0.3	0.2	0.5	2.0	1.0	1.9	0.0	0.7	1.1	0.9	0.9	1.4	0.5	0.6	0.7	0.6
Chr+Tri	0.2	0.3	0.5	0.3	0.6	2.4	1.0	1.9	0.1	5.4	1.2	0.9	0.6	1.0	0.4	0.5	1.0	0.7
1MChr	0.3	0.4	0.6	0.4	0.0	0.1	0.5	0.9	0.0	0.5	1.0	0.8	0.4	0.7	0.3	0.3	0.4	0.3
2MChr	0.5	0.8	0.9	0.6	0.4	1.5	0.6	1.1	0.0	1.7	n.d.	n.d.	0.7	1.2	0.5	0.6	0.8	0.7
3MChr	0.3	0.5	0.7	0.4	0.5	2.0	n.d.		n.d.		1.1	0.9		0.0		0.0		0.0
Sum MChr	1.1	1.7	2.3	1.4	0.9	3.6	1.1	2.0	0.0	2.2	2.1	1.7	1.2	1.8	0.8	1.0	1.2	0.9

Continuation Table 18																		
	MVBC		HVBC1		HVBC2		HVBC3		Ant		HC1		HC2		HC3		FC	
	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum	M	C/Csum
B(b)Flu	n.d.	n.d.	0.2	0.1	0.3	1.2	0.3	0.6	0.1	10.2	0.7	0.6	0.2	0.3	0.1	0.1	0.3	0.2
B(k)Flu	n.d.	n.d.	n.d.	n.d.	0.4	1.4	0.3	0.6	0.1	4.5	0.6	0.4	0.1	0.1	0.0	0.1	0.1	0.1
B(a)Flu	n.d.	n.d.	n.d.	n.d.	0.0	0.0	0.1	0.2	0.0	0.2	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
B(e)Py	0.1	0.1	0.4	0.2	0.0	0.1	0.4	0.7	0.1	5.3	1.1	0.9	0.2	0.3	0.2	0.2	0.7	0.5
B(a)Py	0.2	0.3	0.4	n.d.	0.7	2.8	0.6	1.1	0.0	1.6	1.2	0.9	0.4	0.6	0.3	0.3	0.6	0.5
Per	n.d.	n.d.	n.d.	n.d.	0.5	2.1	0.0	0.1	n.d.		n.d.	n.d.	0.1	0.2	0.0	0.0	0.1	0.0
Indeno	n.d.	n.d.	0.1	0.0	0.0	0.1	0.2	0.4	0.0	3.0	n.d.	n.d.	0.1	0.1	0.0	0.0	0.1	0.1
D(a,h)Ant	n.d.	n.d.	n.d.	n.d.	0.0	0.2	0.1	0.1	0.0	0.6	n.d.	n.d.	0.0	0.1	0.0	0.0	0.1	0.1
B(g,h,i)Per	n.d.	n.d.	0.4	0.2	0.1	0.5	0.5	1.0	0.1	5.8	n.d.	n.d.	0.1	0.2	0.1	0.2	0.7	0.5
Anth	n.d.	n.d.	n.d.	n.d.	0.1	0.3	0.2	0.3	0.0	0.6	n.d.	n.d.	0.1	0.2	0.1	0.1	0.2	0.2
Sum 16EPA PAHs	**22.4**		**50.5**		**6.0**		**12.9**		**0.7**		**28.7**		**9.8**		**22.1**		**37**	
Sum all PAHs	**68.0**		**165.8**		**25.4**		**53.0**		**1.1**		**129.6**		**68.3**		**84.5**		**130.6**	

C) List of Figures

D) List of Tables