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„Pollution of Saxony's topsoils
by polycyclic aromatic hydrocarbons (PAH16) “
Situation Analysis & Evaluation“

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Abstract

A statistical study of polycyclic aromatic hydrocarbons (PAH) in Saxony's topsoils was conducted. 2167 samples were taken from the top humus rich layer (Ø 20 centimeters in depth), the concentrations of the 16 US-EPA PAHs were measured and combined to one data file which was used for evaluation. For analysis, four different demographic and four different land use categories were introduced and used for distinction of: Concentrations (in terms of background values), seasonal variations, a toxicological assessment, humus contents as well as correlations between humus and PAHs. Maps of Benzo(a)pyrene [B(a)P] and the sum of the 16 PAHs were created for the area of Saxony. Concentrations were highest for densely populated and/or recreational green zones of settlement areas. Seasonal variations proved to be clearest for agricultural soils and forest soils showed highest humus contents as well as correlations towards PAHs. The trigger value of 1 mg/kg soil for B(a)P for inhabited areas was not exceeded frequently (25 times) and mostly by city soils as these suffer most from PAH pollution.

Abstrakt

Eine statistische Arbeit über polyzyklische aromatische Kohlenwasserstoffe (PAK) in Sachsens Oberböden wurde durchgeführt. Dabei wurden 2167 Proben von der obersten humusreichen Bodenschicht (Ø 20 Zentimeter tief) genommen. Die Konzentrationen der 16 US- EPA PAKs wurden gemessen und zu einem Excel File zusammengeführt. Dieses wurde im Anschluss zur Datenauswertung verwendet. Während der Evaluierung wurden vier verschiedene demographische, sowie vier verschiedene Landnutzungskategorien eingeführt um das Verhalten der Stoffe differenziert darzustellen. Dabei wurde folgendes näher betrachtet: Die Konzentrationen (In Form von Hintergrundwerten), saisonale Variationen, eine toxikologische Evaluierung, Humusgehalt sowie die Korrelationen zwischen Humus und PAKs. Außerdem wurden Karten von Benzo(a)pyren B(a)P und der Summe PAK (alle 16 PAKs) für das Gebiet Sachsens angefertigt.

Die PAK-Konzentration war am Höchsten in dicht besiedelten Gebieten (Städten) und/oder Siedlungsgrünflächen. Saisonale Variationen waren am deutlichsten bei Ackerflächen zu erkennen und Waldböden zeigten den höchsten Humusgehalt (in Prozent) sowie die stärksten Korrelationen mit PAKs. Der Grenzwert von 1 mg B(a)P pro Kilogramm Boden wurde nicht oft überschritten (25 Mal) wohingegen diese Überschreitungen Großteils in Stadtböden gefunden wurden, da diese am Meisten unter PAK Belastungen leiden.

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1. Extended summary

As the title suggests, this thesis intends to describe the current situation of polycyclic aromatic hydrocarbons (PAHs) in Saxony's topsoils, whereas topsoils are regarded as top soil layer with high organic carbon contents as well as high root densities described as A_h , A_p , A_e , $A_h - A_p$ and $S_w - A_p$ horizons according to German soil classification. (Ad-hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe and Bundesanstalt für Geowissenschaften und Rohstoffe 2005) Typically, these horizons are found within the top 30 centimeters in agricultural, grassland and settlement soils, whereas it is usually less (10cm) in forest soils but may reach down to 46cm. The compound group of interest (PAHs) are a very large group of several hundred compounds that consist out of two or more benzene rings that are fused in a linear, angular or cluster arrangement and are mostly of aromatic electron arrangements, with the exception of cyclopentane centers of Fluorene based PAHs. (Masih and Taneja 2006; Abdel-Shafy and Mansour 2016; Najmeddin and Keshavarzi 2019)

For analysis a large data set of 2167 samples, taken in between the 4th of April 2010 and the 12th of January 2018, was used. This file was provided by the LfULG (Sächsisches Landesamt für Umwelt, Landwirtschaft und Geologie). While many variables were recorded during sampling, the key data evolves around the concentrations of the so called "*16 US-EPA polycyclic aromatic hydrocarbons*". These 16 compounds, namely: Naphthalene (Naph), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (FluA), Pyrene (Pyr), Benzo[a]anthracene (B(a)A), Chrysene (Chry), Benzo(b)fluoranthene (B(b)F), Benzo(k)fluoranthene (B(k)F), Benzo(a)pyrene (B(a)P), Benzo(g,h,i)perylene (B(ghi)P), Indeno(1,2,3-c,d)pyrene (I(c,d)P), and Dibenz(a,h)anthracene (DB(a,h)A) are the most frequently found PAHs and are often described to represent the family of "*polycyclic aromatic hydrocarbons*". (US EPA 2005)

Many PAHs are of interest because of their carcinogenic and mutagenic properties. Out of the 16 PAHs listed by the US-EPA, 8 compounds are recognized as mutagenic and/or carcinogenic and were categorized as 2A or 2B by the International Agency for Research on Cancer (IARC). (Simon et al. 2007) Plenty of international organizations, such as the US-EPA, the ATSDR, WHO-FAO or the SCF-EU created priority lists that focused on different features of PAHs. As mentioned previously the US-EPA focused on abundance, whereas the ATSDR and the SCF-EU emphasized toxicological potencies. (Belis et al. 2011; FAO/WHO 2006; US EPA 2005)

Polycyclic aromatic hydrocarbons are the product of incomplete combustion processes of anthropogenic as well as natural origin. Yet, the lion's share of PAH emissions originates from anthropogenic activity including small combustion plants, engines of private vehicles, coal and coke production and industrial processes. (Callén et al. 2008; Mostert et al. 2010) Because of that, several groups of demography as well as land use practices were used for analysis. In other words: It is expected that concentrations of these compounds will be much higher in proximity to conurbations and industrial areas where PAHs are emitted as byproducts of numerous combustion processes considering that only a few PAHs are synthesized in low quantities for industrial purposes (e.g. Pyrene and Anthracene). (Abdel-Shafy and Mansour 2016; MLUR 2016)

For analysis, statistical programs such as SPSS, Statgraphics and Primer were used to find patterns, variations, clusters and representative functions that help understand the distribution of these compounds and formulate, together with additional knowledge from publications, explanations as for

why pollution levels are distinct. Distinct because the 16 compounds are known to possess quite a few properties that differ on several orders of magnitude. This is especially of interest with regards to properties that govern PAH mobility and behavior such as: volatility, partitioning coefficients, solubility in water and the carbon sorption coefficients. Vapor pressures of these 16 compounds for instance are found in between 10^2 (Naphthalene) and 10^{-8} Pa (Benzo(g,h,i)perylene), solubility in between 31 mg/L and $3 \cdot 10^{-4}$ mg/L and carbon sorption coefficients in between 278 L/kg and 365 000 L/kg. (Paraíba et al. 2011; Lundstedt 2003) Numbers suggest that smaller, and hence lighter PAHs, consisting out of 2 or 3 ring structures, are generally more mobile than heavier, bigger PAHs of 4 or more ring structures. PAHs are also subject to long-range translocation processes, whereas transport bound to particles is of primary importance. Gas-phase PAH concentrations in the Arctic, which is considered to reflect remote territory, are orders of magnitude lower than in Europe, while the concentrations of particle-bound PAHs were found to be only slightly lower. (Lohmann and Lammel 2004)

Based on the physical properties of PAHs, less volatile species like Benzo(a)pyrene and Fluoranthene should not undergo long-range transport at all, (Zelenyuk et al. 2012) but have been found to travel long distances too. Recently, research found that also Benzo(a)pyrene is effectively bound as well as transported with atmospheric particles. (Shrivastava et al. 2017)

Aside from specific properties and behavioral features elaborated in the results section for the area in question (Saxony), the thesis also covers a general introduction that gently guides the reader towards the content by starting with a few general words about Saxony, an explanation of why PAHs are of importance and how (inter)national organizations deal with them.

Following a general information section that covers more specific information. The properties of the 16 PAHs are discussed in detail, including the consequences for partitioning in between particulate, vapor and solid phases for different temperatures and seasons as well as mechanisms for long-range transport.

Also, sources of PAHs are discussed in terms of industrial as well as source branches (pyro- and petrogenic). PAH markers as well as PAH profiles are reviewed that identify PAH sources like fires or combustion engines. These profiles are used to identify distinct wood types or differentiate in between leaves, wood and paper as well as in between particular peat types. (Freeman and Cattell 1990; Samburova et al. 2016) Along with that, factors that influence PAH formation are discussed. These factors include combustion temperature, moisture content of the substrate and oxygen availability.

As toxicological features of PAHs are of major concern, these features: their potency, potency evaluation, the divergence in between theoretically evaluated and observed adverse effects as well as the current legislative guidelines in Germany and suggestions to improve evaluation by international organizations, such as the EFSA (European Food Security Agency), are discussed.

To complete theoretical background information, the thesis includes a chapter about degradation processes, the role of vegetation for pollutant distribution, adsorption as well as deterioration and sinks as well as remediation techniques. This last introductional part is by far the longest, as it moves from general fractionation processes towards most prominent degradation processes including remediation.

Bioremediation techniques discussed are as diverse as the microorganisms mediating them and include: Abiotic loss, which is most prominent for low molecular weight PAHs, indigenous microbial degradation, (Sun et al. 2010) whereas these processes show large result deviations in between laboratory and in situ testing. Next to bacteria numerous fungi, such as arbuscular mycorrhiza fungi (AMF), ectomycorrhizal fungi (EMF), ligninolytic and non-ligninolytic fungi, but also archaea and microalgae (cyanobacteria and diatoms) are known to enhance PAH degradation. Root tissue enhanced dissipation and root-tissue enhanced biodegradation are mostly discussed separate from

microbial degradation processes but are strongly intertwined with them. Root-tissue based interactions rely on plants exudates, mostly enzymes, which assist PAH degradation. Additionally, these processes improve soil structure, aeration, hydrological features and provide easily degradable carbon which is an energy source for microorganisms. (Lu et al. 2011; Yu et al. 2011) Next to bioremediation techniques, chemical remediation techniques are elaborated, whereas the four most popular oxidative reagents, potassium permanganate, activated persulfate, modified Fenton's reagent and Fenton's reagent are compared.

The bioremediation processes mentioned in the beginning of the previous paragraph are happening naturally in soils and are emphasized as this text is concerned with the situation in natural soils. However, PAH degradation processes also occur in vapor and particulate phases, wherein ozone, hydroxyl radicals and nitrite radical mediated degradation as well as photolysis are discussed as these processes also play an important role for PAH input/deposition for soils.

No thesis is complete without elaborating methods, results and discussion. These chapters are found after the theoretical background section and contain what the titles indicate. The methods section describes how the demographic categorizations were selected, takes a deeper look into sampling distribution along these categories as well as land use categories. Also sampling locations and times are displayed in detail, followed by an explanation of what an outlier/extreme value is considering "regular" concentrations as well as for compounds of little abundance, if the 25th and 75th percentiles are to be found at zero/below detection limit. The last part in the methods section explains how toxicological assessments were undertaken and how humus contents were categorized.

The last core section is called results and discussion and contains background value tables of the 50th and 90th percentiles including the number of valid samples by category, boxplots of general PAH abundance, principal components analysis (PCA) – including a graphical representation of the standardized samples, an evaluation of seasonal pattern using low molecular weight PAHs (LMW PAHs) concentrations and relative shares per month for the different land use categories, a deeper look into values of the three conurbations in Saxony, an evaluation of humus contents in Saxony's soils along with correlation analysis for the individual compounds as well as a discriminant analysis (DA), a toxicological assessment and two maps of Saxony, displaying the concentrations of Benzo(a)pyrene (B(a)P) and the concentration of the PAH sum (16 US-EPA PAHs) (sum PAH).

After these sections the thesis ends with a recommendation for future work and acknowledgements.

2. The aim of the theses

This text aims to describe the current situation of Saxony's topsoils regarding polycyclic aromatic hydrocarbons as detailed as possible. That includes:

1. A general description of concentrations found at sampling locations & attempt to create an understanding for their occurrence by reasoning with the current state of knowledge provided by the scientific community.
2. Explain the findings and display the results as vividly as possible & to do so, use all tools that modern statistical programs have to offer.
3. Create two maps presenting the concentrations of a. Benzo(a)pyrene [B(a)P] and b. the sum of PAHs to illustrate the distribution of polycyclic aromatic hydrocarbons

4. Investigate the toxicological situation regarding PAHs within Saxony's borders and examine if all prerequisites for the so called "surrogate marker approach" hold for the data set in question.

3. Introduction

a. The area of assessment – Saxony

Saxony (officially the Free State of Saxony) is a state in the east of central Germany. It shares borders with four other German states as well as Poland and Check Republic. Its topographical features can be subdivided into lowlands-, hilly terrain and low mountain ranges. The states lowest point is situated 73 meters above sea level and is located at the states north border towards Brandenburg, while the highest peak (Fichtelberg) reaches up to 1215 meters and is to be found in the central ore mountains (Erzgebirge) at the states southern border with Check Republic.

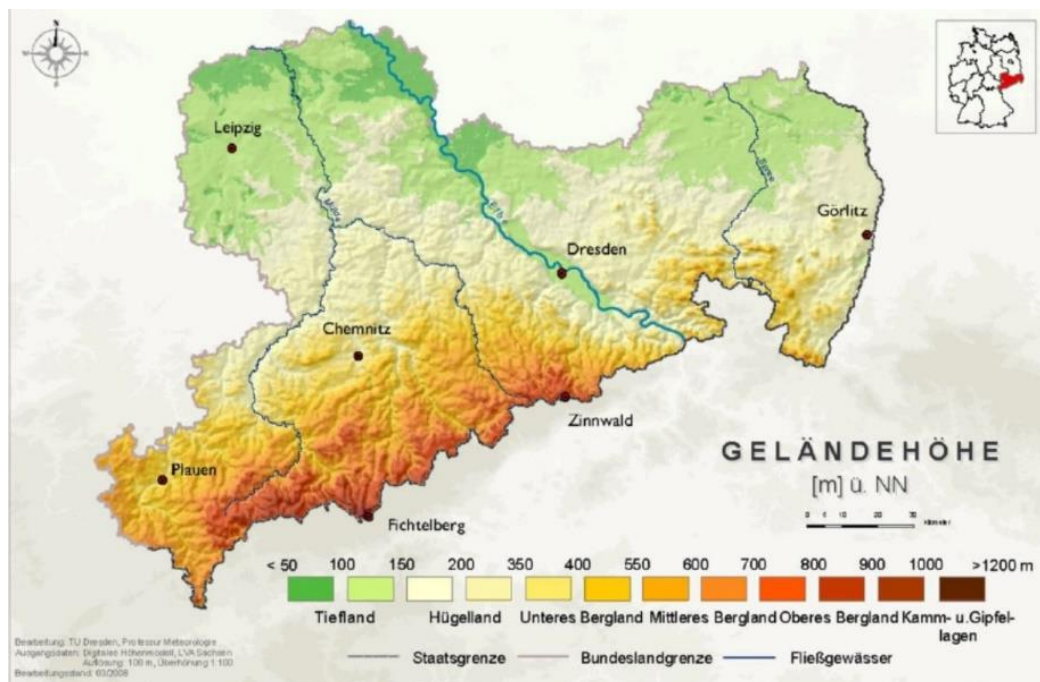


Figure 1: Relief map of Saxony as published by the LfULG (2015)

Figure 1 is a map of the free state of Saxony. It displays its elevation, the location of conurbations as well as rivers situated within its borders. (LfULG, 2015) The state has an area of 18450 km² and three major cities, namely Dresden, Leipzig and Chemnitz within its area. Most of the surface (83%) is covered with vegetation, followed by settlement structures (10,2%), traffic structures (4,4%) and finally 2,4% water bodies. The majority of the first category is dedicated to agricultural land (65,9%), the remaining land to forests (32,3%). The mean annual precipitation and temperature strongly depend on the respective region and are decidedly tied to elevation. For instance: The mean annual precipitation of the weather station Dresden-Klotzsche is 421mm, while its double that amount (943mm) at Fichtelberg. The same pattern can be observed for temperatures: 11,1°C for Dresden-Klotzsche and 5,2°C for Fichtelberg. (Statistik Sachsen 2017, 2019a, 2019b) This has considerable

consequences for the pollutant distribution discussed within this thesis due to the climate linked occurrence of the pollutants in question (PAHs).

Saxony is one of the so-called “*new states*” of Germany: “*New states*” are the ones that used to be part of the GDR (German Democratic Republic) and were reincorporated in 1989, after the fall of the Berlin wall. However, these ex GDR states had a different understanding and legislation concerning pollutant emissions, environmental policy and personal handling of pollutants. A comparative study by the German EPA investigated 1-Hydroxypyrene concentrations (a deteriorate of pyrene and one of the compounds investigated within this thesis) in urine samples of two groups: adults and children. Initial samples for both groups were taken in the years 1990/92, whereas consecutive samples were taken in 1998 (adults) and 2003/2006 (children). The “*new states*”, compared to the “*old states*” displayed 1-Hydroxypyrene concentrations almost 3 times as high for adults and roughly double the amount for children in the years 1990/92, whereas concentrations in children strongly exceeded the ones for adults.

Comparative values in 1998 and 2003/06, did not display such a strong difference between the “*old*” and “*new*” states. Yet, concentrations found in inhabitants of the “*new states*” were still higher in both groups: Adults (~20 ng/L) and children (~40 ng/L) (Umweltbundesamt 2016)

Even though the emissions have dropped significantly in the past decades, the current premises suggest that the so-called “*new-states*” are still more polluted than the “*old states*”, because according to (Keyte et al. 2013) much of the soil PAH content of temperate regions is based on historic accumulation. However, to prove or disprove those premises a thorough investigation for Saxony becomes necessary. This thesis will contribute to create such a comparable data set.

b. Polycyclic Aromatic Hydrocarbons (PAHs) – An Explanation

“*Polycyclic aromatic hydrocarbons are organic compounds*” (p.1) (Bamforth and Singleton 2005). They consist out of two or more benzene or cyclopentadiene rings, whereas these rings are fused in a linear, angular or cluster arrangement. (Masih and Taneja 2006) The Fluorene based PAHs additionally contain a cyclopentane molecule in their center that does not necessarily have an aromatic electron configuration. Their only constituents are carbon and hydrogen while degradation intermediates often include heteroatoms or functional, that are mostly oxygen (OPAH) or nitrogen based (NPAH). (Haritash and Kaushik 2009; Kadri et al. 2017; Marino et al. 2000)

Their nomenclature is based on the IUPAC system (International Union of Applied and Pure Chemistry) but has undergone considerable changes within the last century. Ehrenhauser et al. 2015 argued that this is mostly because IUPAC names can become quite burdensome for large PAHs. The semi-trivial names on the other hand, that are used today, are comparably handy. These names originate from the molecules parent compound, i.e. “*polyacenes*”, “*polyaphenes*”, “*polyphenylenes*”, and “*polynaphthylenes*”. However, for most PAHs there is still more than one name used in current literature. (Ehrenhauser 2015) Within this thesis, the names, as listed in Table 1 will be used.

They typically have high boiling points as well as high melting points and low vapor pressure making them solid under standard conditions. They are mostly colorless, white, or pale-yellow, ubiquitous as well as persistent in the environment and constitute a group of several hundred compounds. (Abdel-Shafy and Mansour 2016) Depending on the compound, they are considered semi-volatile to chemically stable and hydrophobic molecules. However, their volatility and solubility are strongly tied

to the molecular mass, whereas lighter molecules are more volatile and soluble. Thus, their solubility in water ranges from 0,3 (Benzo(ghi)perylene) to 31700 (Naphthalene) $\mu\text{g}\cdot\text{L}^{-1}$. (MLUR 2017; Abdel-Shafy and Mansour 2016)

PAHs are unavoidable side-products of incomplete combustion processes. The amount of PAHs that are produced is strongly depending on the available oxygen, the burning temperature, the substrate itself and their moisture content. (Mastral et al. 1996; MASTRAL et al. 1999; Lu et al. 2009)

Only a few PAHs are synthesized for industrial purposes. Pyrene and Anthracene for instance are used commercially as agricultural or photographic products, thermosetting plastics, lubricant materials, and intermediates in pharmaceuticals. (Abdel-Shafy and Mansour 2016; MLUR 2016) Since it is compulsory in Germany to report PAH usage according to PRTR regulations (Pollutant Release and Transfer Register), PAH release by industrial processes is public knowledge. In the year 2010 for instance, 4170 metric tons were exhausted as gas and another 50,4 metric tons were released to waterbodies, mostly through waste water treatment plants and diffuse inputs such as erosion. (Umweltbundesamt 2016) However, the contribution of non-industrial inputs, such as the exhaust of diesel engines, engine lubricants, the abrasion of car tires or household combustion systems including re-popularizing wood burning fireplaces remain unknown. (IARC 2012, 6/12/2012)

Eventually PAHs that are emitted as gas, either adsorbed on aerosols, particles or as free molecules, will settle and accumulate in soils and through the food chain. This makes PAH contamination mostly the result of long term pollution in regions of constant input from at least several years to decades. (Cachada et al. 2019) The vegetation of the soil in question can play a major role for the accumulation process. Some plants are known to extract persistent PAHs from soils, while others have no or even inhibitory effects due to enhanced retention capacities of roots in the rhizosphere (Liste and Alexander 2000) Also, tree, shrub, herb and woodland vegetation covers are known to trap more airborne PAHs and subsequently accumulate more PAHs in soil than grassland. This phenomenon is based more on the vertical profile of the vegetation cover rather than on plant physiology. The high vertical profile of shrub, herb and woodland offers more surface to capture airborne PAHs, while the deposition in grassland is based entirely on direct deposition. In other words: Larger canopies and diversified species composition enhance interception of airborne PAHs. (Peng et al. 2012)

Because of their carcinogenic, teratogenic and mutagenic features as well as their environmental pollution capacities PAHs have become a major category of urban pollutants. (Cao et al. 2019)

According to CVUA (information services on chemical and veterinary investigation offices, Germany), almost half of PAH uptake by humans is attributed to ingestion. (Dr. Andreas Zeddel 4/27/2017) Smoked and grilled dishes but also cacao and chocolate may contain elevated levels of PAHs and thereby constitute a relevant uptake pathway for the human organism. (Umweltbundesamt 2016)

Another significant uptake mechanism is dermal contact with rubber or soft PVC products, produced with PAH based softeners or plasticizers. In addition to the rubber, they often contain a bulking agent together with PAH containing softening oils, such as creosote or industrial soot. These softeners are noticeably cheaper compared to alternative softeners with no or low PAH contents which makes them very attractive for large-scale manufacturers. TÜV Rheinland AG published sampling results that revealed elevated levels of PAHs in products like handles of tools or bicycles, shoes or sports articles. Some of them exceeded guideline values more than 100-fold. (Umweltbundesamt 2016) (TÜV 2009)

Because of the potentially harmful features of PAHs, many international organizations as well as research institutions and individual states or state unions around the globe have introduced threshold values for what they consider priority PAHs in legislative frameworks. Regarding the research area within this thesis, the ones concerning Germany on an international level are these:

1. REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) which regulates PAH thresholds in consumer goods. REACH generally prohibits the sale of mixtures, such as paints containing carcinogenic, mutagenic or reprotoxic compounds (CMR compounds) to consumers.
Tradable goods as the ones previously mentioned, like rubber or PVC based products, are excluded from these regulations. However, threshold values for toxic PAHs including B(a)P in absolute and relative contents were put in place, wherein the previously mentioned softening oils for e.g. tires are not allowed to be used in case they contain 1 mg/kg B(a)P or more. Also, they must not contain more than 10 mg/kg of PAHs combined. (REACH 2006)
2. The European Parliament and the European council introduced thresholds for PAH release to air, soil and drinking water in their persistent organic pollutant (POP)-regulation first published in 2004 and revised in 2019. (EU Parliament and Council 2019)

National regulations additionally reduce emissions for B(a)P to 0,15 g/hr or 0,05 mg/m³ according to their framework directive on air (BMU 2002), while the European Union chose a different approach, setting an indicative limit value of 1 ng/m³ as air content threshold. (Keyte et al. 2013)

In German soils, initial threshold values were set to 2 mg per kilogram soil for playgrounds, 4 mg/kg in residential areas, 10 mg/kg in parks and public green spaces and 40 mg/kg in industrial and commercially used soils according to an executive order passed in 1999. (Bundesministerium der Justiz und für Verbraucherschutz 7/12/1999)

As of now, German federal states and key organizations such as ALA (Altlastenausschuss) or LABO (Bund/Länder Arbeitsgemeinschaft Bodenschutz) agree that these values were set to high and a reduction is indispensable. Some states (e.g. Schleswig Holstein and Bavaria) have already passed decrees that reduce these threshold values to 0,5 mg/kg in playgrounds, 1 mg/kg in residential and recreational areas (e.g. parks) and 5 mg/kg in industrial soils. (MLUR 2017) However, these decrees can only address local departments and do not include legal consequences in case these values are exceeded. A reduction of these values to the ones listed in this paragraph as executive order is scheduled for the next amendment of the current soil protection law (BBodSchV – Bodenschutzverordnung 1999 556/17).

Benzo(a)pyrene is often used as reference substance for complex PAH – mixtures, because it is by far the best characterized PAH and correlates strongly to other PAH concentrations. (Petry et al. 1996) However, it was argued recently that the current B(a)P based assessment method for the toxicological relevance is insufficiently accurate to ensure human safety. (EFSA 2008) The European Food Security Agency (EFSA) proposed and assessed different approaches wherein more than one compound (B(a)P) was quantified and used for the evaluation of relevant toxicity. (EFSA 2008) In 2011 EU regulations on PAH assessment in food was amended, stating a respective maximum level not only for Benzo(a)pyrene but also for the sum of four PAHs (PAH₄), namely: Benzo(a)pyrene, Chrysene, Benzo(a)anthracene and Benzo(b)fluoranthene, based on the conclusions of the research by the

EFSA's Panel on Contaminants in the Food Chain (CONTAM). (Schulz et al. 2014; EU comission No 835/2011)

c. What are Priority PAHs and what makes them a priority substance?

Out of the several hundred PAHs that are known to scientists today, a few have been labeled “*High Priority Pollutants*” by e.g. the US-EPA. (Hussar et al. 2012)

Depending on the organization classifying these PAHs as “*High Priority Pollutants*”, different features were emphasized. In that context, the 16 US-EPA-PAHs were identified as the most frequently encountered PAHs in environmental samples. Out of those 16 PAHs, half are considered mutagenic and/or carcinogenic and were categorized as 2A or 2B by the International Agency for Research on Cancer (IARC). (Simon et al. 2007) The group 2A constitutes compounds that are probably carcinogenic to humans while the group 2B holds compounds that are possibly carcinogenic to humans. A compound labeled as Group 3, it not classifiable as carcinogenic according to the IARC.

The European Commission's Scientific Committee on Food (SCF) evaluated 33 different PAHs and classified 7 other PAHs as of “*major concern to human health*”. (Simon et al. 2007) Those 7 additions, 7 out of the 8 IARC US-EPA PAHs, with the exception of Naphthalene and in addition of Benzo(g,h,i)perylene were subsequently referred to as the 15 EU priority PAHs. In 2005, the joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additive added another compound to the list, namely: benzo[c]fluorene (EU comission No 108/EC/ 2005) and one year

Compound	Abbreviation	IARC - Group	Year	Volume	US-EPA	SCF-EU
Benz(a)anthracene	B(a)A	2A	2010	92; Sup 7	✓	✓
Benzo(a)pyrene	B(a)P	2A	2012	92; 100F; Sup 7	✓	✓
Dibenz(a,h)anthracene	D(a,h)A	2A	2010	92	✓	✓
Benzo(b)fluoranthene	B(b)F	2B	2010	92	✓	✓
Benzo(k)fluouranthene	B(k)F	2B	2010	92	✓	✓
Indeno(1,2,3-c,d)pyrene	I(c,d)P	2B	2010	92; Sup 7	✓	✓
Chrysene	Chry	2B	2010	92	✓	✓
Naphthalene	Naph	2B	2002	82	✓	
Anthracene	Anth	3	2010	92; Sup 7	✓	
Fluoranthene	FluA	3	2010	92; Sup 7	✓	
Phenanthrene	Phen	3	2010	92; Sup 7	✓	
Pyrene	Pyr	3	2010	92; Sup 7	✓	
Benzo(g,h,i)perylene	B<(ghi)P	3	2010	92; Sup 7	✓	✓
Fluorene	Flu	3	2010	92; Sup 7	✓	
Acenaphthylene	Acy	No Data	-	-	✓	
Acenaphthene	Ace	3	2010	92	✓	
Cyclopenta(c,d)pyrene	CCP	2A	2010	92; Sub 7		✓
Dibenzo(a,l)pyrene	D(a,l)P	2A	2010	92; Sub 7		✓
Dibenzo(a,h)pyrene	D(a,h)P	2B	2010	92; Sub 7		✓
Dibenzo(a,i)pyrene	D(a,i)P	2B	2010	92		✓
Benzo(j)fluoranthene	B(j)F	2B	2010	92		✓
5-Methylchrysene	5-MC	2B	2010	92; Sub 7		✓
Benzo(c)fluorene	B(c)F	3	2010	92; Sub 7		✓/+1
Dibenzo(a,e)pyrene	D(a,e)P	3	2010	92; Sub 7		✓

Table 1: List of the names and abbreviations of the most commonly found PAHs on priority lists. Followed by their IARC classification, including their publication Volume and year. The last two columns indicate their listing on either or both priority lists, namely: US-EPA and or SCF-EU/JECFA/FAO-WHO

later concluded, that the 15 PAHs previously mentioned, are clearly genotoxic (FAO/WHO 2006) Nowadays, literature refers to these compounds as the “15 + 1 EU-PAHs”.

Table 1 displays the individual PAHs that were deemed “priority” by the formerly mentioned institutions, their IARC classification as well as the year of assessment by the IARC.

In a nutshell: The prioritization by the US-EPA is mostly based on the abundance of PAHs found in environmental samples, while the EU focused on the toxicity of those compounds. Eight of those compounds are to be found on both lists. These compounds are both, carcinogenic and comparatively abundant. Apart from carcinogenicity, European legislative institutions added compounds that were additionally genotoxicity and/or mutagenic, emphasizing not abundance in the environment but their harmful features.

For the purpose of this thesis, the so-called “16 EPA PAHs”, namely: Naphthalene (Naph), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (FluA), Pyrene (Pyr), Benzo[a]anthracene (B(a)A), Chrysene (Chry), Benzo(b)fluoranthene (B(b)F), Benzo(k)fluoranthene (B(k)F), Benzo(a)pyrene (B(a)P), Benzo(g,h,i)perylene (B(ghi)P), Indeno(1,2,3-c,d)pyrene (I(c,d)P), and Dibenz(a,h)anthracene (DB(a,h)A) are primarily considered and therefore thoroughly analyzed and discussed.

d. Properties of PAHs

As shortly addressed in the introduction, PAHs are semi-volatile compounds and will thus appear in vapor and condensed phases, when exhausted by incomplete combustion processes. Eventually PAHs in the atmosphere (vapor phase) will be deposited to soils. According to (Keyte et al. 2013) dry deposition is a more effective removal process from the atmosphere than wet deposition regarding the more hydrophobic gaseous PAHs. However, PAHs are also omnipresent in remote areas which indicates long-range translocation processes. This makes the atmospheric chemistry of these compounds particularly important as it governs their atmospheric lifetime and subsequently their dispersion as well as distribution.

The separation in vapor and condensed phases is often expressed with the gas-particle partitioning coefficient, which is greatly influenced by ad- as well as ab-sorption processes, vapor pressure and is thus strongly temperature dependent. However, other factors such as the particle properties which includes size, distribution, organic carbon content as well as the amount of “total suspended particles” but also wind speed, humidity and pressure (altitude) play an important role for the partitioning process. (Tasdemir and Esen 2007) Additionally, geographical features must be taken into account. In coastal regions for instance, factors such as circulations between land and sea, maritime airflows and exchange processes between air and water have to be considered. (Lai et al. 2011) In mountain regions, the exposition and slope do play a role, wherein north oriented slopes, in the northern hemisphere, show a higher PAH concentration due to lower photoperiods and the resulting minor daily light integral. (Tremolada et al. 2009) This makes the modelling of gas-particle partitioning coefficients a complex endeavor as all of these factors influence the process of partitioning.

Consequently, multimedia fugacity and atmospheric dispersion models become a powerful tool to attempt the quantification of air-soil exchange processes and conclude removal as well as contamination processes of soil and air. (Wang et al. 2011)

There is a strong interrelationship between the molecular weight of the PAHs and their solubility as well as vapor pressure. Table 2 displays the 16 EPA PAHs, the number of rings constituting these

compounds, their molecular weight in, solubility and vapor pressure. Most values were extracted from Lundstedt et al. 2003 with two exceptions taken from Paraíba et al. 2011 marked with a star (*).

	N° of rings	Molecular Weight [g/Mol]	Solubility in H2O [mg/L]	Vapor pressure [Pa]
Naphthalene	2	128	31	$1,0 \cdot 10^2$
Acenaphthylene	3	152	16	$9,0 \cdot 10^{-1}$
Acenaphthene	3	154	3,8	$3,0 \cdot 10^{-1}$
Fluorene	3	166	1,9	$9,0 \cdot 10^{-2}$
Phenanthrene	3	178	1,1	$2,0 \cdot 10^{-2}$
Anthracene	3	178	$4,5 \cdot 10^{-2}$	$1,0 \cdot 10^{-3}$
Pyrene	4	202	0,13	$6,0 \cdot 10^{-4}$
Fluoranthene	4	202	0,26	$1,2 \cdot 10^{-3}$
Benzo(a)anthracene	4	228	$1,1 \cdot 10^{-2}$	$2,8 \cdot 10^{-5}$
Chrysene	4	228	$6,0 \cdot 10^{-3}$	$5,7 \cdot 10^{-7}$
Benzo(b)fluoranthene	5	252	$1,5 \cdot 10^{-3}$	$6,7 \cdot 10^{-5*}$
Benzo(k)fluoranthene	5	252	$8,0 \cdot 10^{-4}$	$5,2 \cdot 10^{-8}$
Benzo(a)pyrene	5	252	$3,8 \cdot 10^{-3}$	$7,0 \cdot 10^{-7}$
Dibenzo(a,h)anthracene	6	278	$6,0 \cdot 10^{-4}$	$3,7 \cdot 10^{-10}$
Indeno(1,2,3,c,d)pyrene	6	276	$1,9 \cdot 10^{-4}$	$1,7 \cdot 10^{-8*}$
Benzo(g,h,i)perylene	6	276	$2,6 \cdot 10^{-4}$	$1,4 \cdot 10^{-8}$

Table 2: Number of Rings, molecular weight, aqueous solubility and vapor pressure in absolute numbers of the 16 EPA PAHs. Numbers were extracted from: (Lundstedt 2003); Values marked with * were extracted from (Paraíba et al. 2011)

(Lundstedt 2003; Paraíba et al. 2011)

Low molecular weight PAHs show higher water solubility and higher vapor pressures than high molecular weight PAHs. With increasing molecular mass, the solubility and the vapor pressure decrease gradually.

René P. Schwarzenbach published an article in the handbook for environmental chemistry in 1993, wherein the relationship between the vapor pressure and molecular weight was investigated. According to the published graphical evaluations, the molecular weights of Naphthalene, Fluorene, Phenanthrene, Fluoranthene, Anthracene, Pyrene, Benzo(a)anthracene and Benzo(a)pyrene correlated strongly to negative natural logarithms of vapor pressures at 25°C with a considerable correlation coefficient of 0,9017 underlining the interrelationship previously mentioned. (Schwarzenbach et al. 2017)

In other words: PAHs with lower vapor pressures, like Benzo(a)pyrene, will tend to adsorb on particles, while PAHs with higher vapor pressures, such as Naphthalene will predominantly be found in the vapor phase. Therefore concentrations in the gas phase rise during summer months – or generally in tropical - hot regions – and vice versa for the colder winter months or generally in arctic regions. (Wang et al. 2009; Abdel-Shafy and Mansour 2016)

As indicated shortly, the chemistry of the suspended particles has great influence on the adsorption process of PAHs on those particles. Often, PAHs and suspended particles do occur proportionately because of shared emission sources, such as the burning of fossil fuels and Volcanic eruptions. (Omidvarborna et al. 2015; PUESCHEL and MENDONCA 1972)

A study conducted by (Lai et al. 2011) investigated the seasonal variability of PAHs, the composition of the PAHs in the vapor phase as well as their relationship to the total suspended particles measured in Coastal Park – SW Taiwan. According to their results, the measured “total suspended particles” correlated strongly to PAH concentrations. Yet, an exception was found and explained by the authors.

During August, so the authors argue, a religious tradition in Taiwan – “Ghost Month” – took place, during which joss paper and incense burning is customary. That is why PAH concentrations rise disproportionately higher compared to the other months displayed.

The results also show higher concentrations in winter months (Dec – Feb) compared to summer months (Jun – Aug). However, this phenomenon is not governed by temperature dependent volatilization rates but by wind patterns. During summer, the monsoon over southern China and the southern Chinese sea enhances convection and dispersion of suspended particles (also referred to as “total suspended particles” TSP) and PAHs, while the wind direction during winter brings PAH containing air masses from the islands interior.

Furthermore, 76% of total PAHs were accounted for as gas, while only 24% were found in the particulate form. The constitution of the two forms was further investigated. The lion shares of 2, 3 and 4 ring PAHs were found in their vapor form, whereas 5 ring PAHs were found mostly as particulates and 6 as well as 7 ring PAHs were found exclusively in their particulate form. That goes right along with what was explained earlier. More volatile – low molecular PAHs will be found mostly as gas, while the less volatile – high molecular PAHs are more commonly found as particulate.

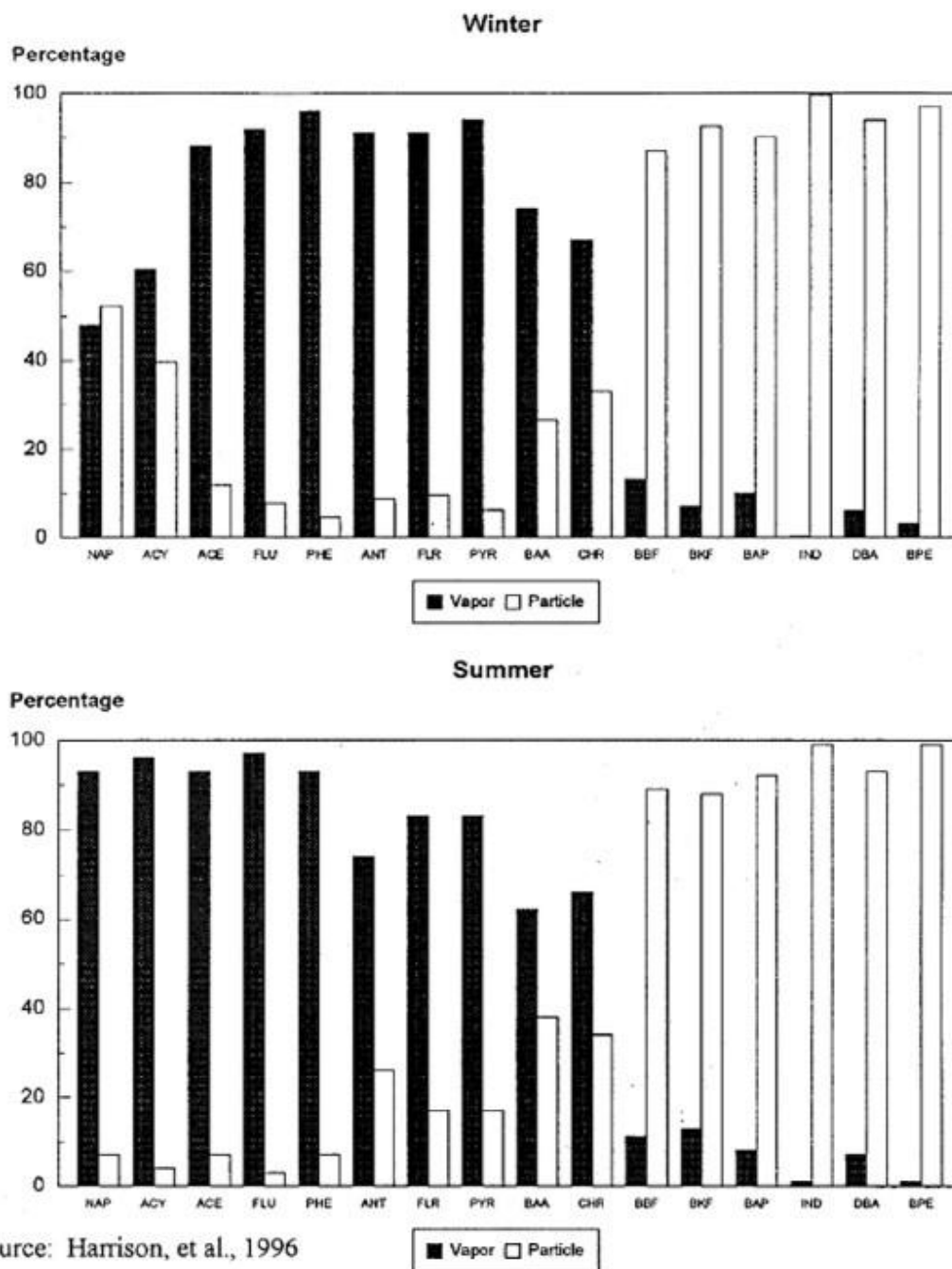
PAHs emitted or evaporated from a source into the atmosphere will eventually reach an equilibrium between phases depending on local temperature, vapor pressure of PAHs and concentrations of the total suspended particles.

A comprehensive study by (Tasdemir and Esen 2007) characterized PAH concentrations in the gas as well as in the solid phase, in the city of Bursa. Compared to Coastal Park, Bursa has no considerable geographic features nor dominant wind patterns that enhance PAH dispersion. This allows the authors to state, that the PAH concentrations were mainly based on traffic and industrial activities of the region. The results highlighted again, that low molecular weight PAHs are mainly occurring as a gas. This time, in greater detail though, since the compounds were listed and evaluated individually and can be compared to vapor pressure values and molecular masses. Furthermore, the study attempted to correlate the PAH concentration with temperature data but was not able to establish a significant relationship in between the two.

On one end Naphthalene, as the only representative of 2-ring PAHs, was found exclusively in its vapor form, while, in contrast, the three 6-ring based PAHs, Dibenzo(a,h)anthracene, Indeno(1,2,3-c,d)perylene and Benzo(ghi)perylene were almost exclusively found as particulates. The 3, 4 and 5-ring based PAHs are located in between the two extremes. Other low molecular weight PAHs with 3 ring structures, namely Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene and Anthracene were predominantly found in the vapor phase, whereas Fluoranthene, Pyrene, Benzo(a)anthracene and Chrysene were almost evenly distributed between the two phases.

Other studies, in Greece, Spain, China, Italy and the U.K. went one step further and evaluated the seasonal variability of PAHs in air including the corresponding rising and falling temperatures that go along with it. (Tsapakis and Stephanou 2005; MASTRAL et al. 2003; Lang et al. 2007; Valerio and Pala 1991; Harrison et al. 1996)

Figure 2 shows the results of a study conducted by (Harrison et al. 1996), that were later transformed into a graph by (Abdel-Shafy and Mansour 2016), from where it was extracted. The sampling took place in Birmingham, central U.K. The samples for “Winter” were taken in February and the ones for “Summer” in August. The figure demonstrates what was indicated previously: The volatility/partitioning of the 16 EPA PAHs and the dependency on seasons and therefore temperature.



Source: Harrison, et al., 1996

Figure 2: Illustration of the particle/vapor PAH distributions from winter to summer. (Abdel-Shafy und Mansour 2016)

Again, PAHs with lower vapor pressures are affected more intensely than the ones with higher vapor pressure. In any case, the difference in between the seasons is significant. Especially Naphthalene, as the most volatile representative for PAHs, is almost exclusively found in the vapor phase during summer months. More graphs, similar to this one, can be viewed in the papers referred to at the beginning of this paragraph.

So far, this chapter illustrated the sorption behavior of PAHs when in air and as particulate. As mentioned previously, these properties govern the long-range transport and distribution of PAHs, especially for the more volatile compounds. (Keyte et al. 2013) However, soils are major sinks for persistent organic pollutants (POPs) such as PAHs, due to their strong affinity to soil organic matter

(SOM). Also the toxic effects of these compounds is strongly influenced by bioavailability. (Cabrerizo et al. 2011; Yang et al. 2010)

In fact, only a small fraction is bioavailable while the lion's share is sequestered and undegradable as well as unavailable for re-volatilization due to the strong interactions with SOM or diffusion into nano-scale pores. (Barriuso et al. 2008) This is why PAHs can be adsorbed easily onto soil organic matter particles and thus form persistent micropollutants. (Gan et al. 2009)

Consequently, the amount of soil organic matter and the pore size distribution have a great influence on the partitioning process between soil and air, as well as between soil and water, while the sorption process is often explained with hydrophobic interactions in between PAHs and SOM. (Karickhoff 1981; Ahmad Gholamalizadeh Ahangar 2010)

Additionally, research suggests, that not only SOM content but also its quality – often related to as aromatic content – influences the sorption capacity. The binding process to humic substances (HS), which have a high aromatic content and constitute about 50 to 80% of natural organic matter in water and soil, leads to increased mobility of those micropollutants while the binding affinity to HS for PAHs is often expressed as soil adsorption coefficient (K_{oc}) and is related to the structure and composition of HS.. (Perminova et al. 1999)

Table 3 shows values of: the octanol-water partition coefficient ($\log K_{ow}$) as natural-logarithm, half-life in the soil ($t_{1/2}$) and the soil organic carbon sorption coefficient (K_{oc}). The numbers were extracted from a paper published in 2011 (Paraíba et al. 2011) that investigated soil contamination by PAHs from sewage sludge.

	N° of rings	Log K_{ow}	$t_{1/2}$ [days]	K_{oc} [L/Kg]
Naphthalene	2	3,3	48	278
Acenaphthylene	3	3,9	60	1054
Acenaphthene	3	3,9	102	1011
Fluorene	3	4,2	60	1737
Phenanthrene	3	4,5	200	3111
Anthracene	3	4,4	460	3046
Fluoranthene	4	5,1	440	11787
Pyrene	4	4,9	1870	7456
Benzo(a)anthracene	4	5,8	670	46563
Chrysene	4	5,8	990	51670
Benzo(b)fluoranthene	5	5,8	610	48542
Benzo(k)fluoranthene	5	6,1	2140	96481
Benzo(a)pyrene	5	6,1	530	100582
Indeno(1,2,3,c,d)pyrene	6	6,7	730	329458
Dibenzo(a,h)anthracene	6	6,7	940	365595
Benzo(g,h,i)perylene	6	6,6	650	284787

Table 3: Values of the 16 US-EPA: Logarithmic partitioning coefficient between octanol and water (K_{ow}), solubility in water (S_w), vapor pressure (V_p), half-life in soils given as days ($t_{1/2}$) and organic carbon sorption coefficients (K_{oc}) (Paraíba et al. 2011)

It contains values for octanol-water partitioning and organic carbon sorption coefficient as well as a half-life value as evaluated by the study. Naturally, the octanol-water coefficient is inversely related to the solubility of the compounds, though it reveals more information. It is a direct measure for the partitioning process in between water and octanol – a hydrophobic oil like substance - as well as the

hydrophobicity of the compound and often used as relative indicator of the tendency of an organic compound to adsorb to soil and living organisms.

As mentioned earlier, sorption is based on hydrophobic interactions, therefore high molecular weight, less soluble, less volatile, hydrophobic PAHs with high $\log K_{ow}$ values, such as Benzo(ghi)perylene are sorbed more efficiently onto soil organic matter compared to low molecular, more soluble, more volatile, less hydrophobic PAHs with lower $\log K_{ow}$ values, such as Naphthalene. This is why typically, the carbon sorption coefficient and the octanol water partitioning coefficient are strongly linked to each other.

Note, that this relationship may predict sorption behavior but is not to be confused with an absolute scale. A study by (Perminova et al. 1999) compared the sorption behavior of Pyrene, Fluoranthene and Anthracene at different humic acid concentrations and created a correlation analysis for these substances. Their results showed that Anthracene, with a $\log K_{ow}$ value of 4,4 constituted the lower end of sorption behavior, Fluoranthene was found in the middle, with a $\log K_{ow}$ value of 5,1 and finally Pyrene, with a $\log K_{ow}$ value of 4,9 on the upper end. The K_{oc} value of Fluoranthene is much higher compared to Pyrene, which should lead to greater adsorption rates for Fluoranthene if $\log K_{ow}$ values are considered only.

Furthermore, sorption also depends on the quality and quantity of humic acid, and that sorption values, such as the K_{oc} and K_{ow} only indicate estimates of sorption behavior. Also, as implied earlier, sorption greatly influences degradation processes that will be further discussed in greater detail within the chapter *“3g Degradation, the role of vegetation, remediation and sinks”*.

As mentioned in the introduction of this chapter, PAHs are subject to long-range translocation processes. Since PAHs show diverse vapor pressures over several orders of magnitude, (Lundstedt 2003; Paraíba et al. 2011) the process does not affect all PAHs equally nor in the same way.

Because of its vapor pressure Naphthalene is almost exclusively found as gas under atmospheric conditions, while re-volatilization applies for most 3 to 4 ring PAHs, which are considered semi-volatile if the vapor pressure is in the range of 10^{-2} and 10^{-6} Pa. (Keyte et al. 2013) These semi-volatile substances may be re-volatilized from surfaces such as vegetation, soils and water, adsorbed onto particles and subsequently transported. In that context the gas exchange promotes long range transport, due to secondary emissions and the partitioning induced by it. (Keyte et al. 2013; Tamamura et al. 2007)

It seems, that long-range transport is mainly accounted for by particle-bound migration. A study by Lohmann et al. in 2004 revealed, that the gas-phase PAH concentrations in the Arctic, which is considered to reflect remote territory, are orders of magnitude lower than in Europe, while the concentrations of particle-bound PAHs is only slightly lower than in Europe. (Lohmann and Lammel 2004)

However, the transport process may be prevented by either (photo)degradation or deposition, whereas dry deposition is more efficient than wet deposition regarding hydrophobic gaseous PAHs. Yet, the mechanisms of long-range translocation processes are poorly understood due to a lack of knowledge regarding aerosol partitioning processes and (chemical) loss rates by the two aforementioned counter processes. (Managing Agricultural Greenhouse Gases 2012; Shrivastava et al. 2017; Keyte et al. 2013) Based on the hitherto accepted concepts about the partitioning process between gas and particles, less volatile specimens like Benzo(a)pyrene and Fluoranthene should probably not undergo long-range transport at all. (Zelenyuk et al. 2012)

Only recently, researchers found that also Benzo(a)pyrene, as one of the less volatile PAHs, is effectively bound and transported with atmospheric particles, whereas coating mechanisms and the nature of these coatings were the missing piece to more realistic atmospheric B(a)P distribution models. In 2017 (Shrivastava et al. 2017) published an article and reported to have found an answer to this problem. The coating of these particles with secondary organic aerosols shields them from being oxidized which increases their lifetime significantly and that the oxidation products are being lost rather than staying bound on the particle is the missing link. Additionally, it is important to know, that the adsorption and therefore transport process is not independent of particle size. Studies suggest, that a higher number of different PAHs as well as a higher amount of PAHs are adsorbed onto smaller particles (PM_{2.5}) rather than bigger ones (PM₁₀), whereas the particle emission and therefore also the transport capacity is season dependent. (Ray et al. 2019)

However, the size of the particles seems to have little to no influence on the travel capacity of these particles. The PAHs adsorbed onto these particles can be analyzed and compared to PAH isomer profiles, which will be discussed in chapter “3e sources”, and allows to determine the origin of these compounds when additionally compared to wind direction as well as wind speeds. Wherein this data is used in backward trajectory models and the results are compared to PAH profiles. A study by (Tamamura et al. 2007) detected PAH rich particles in Kanazawa (Japan) that travelled 1000 – 6500km from different sources onto the island. Three pathways that ended in the catchment area for different (end)dates were determined and graphically evaluated. Depending on the date, the catchment area of origin changed several hundred kilometers.

Conclusively, it is safe to say that partitioning between vapor and particulate phases is complex and many factors have to be internalized, while interaction processes between different factors and variables is poorly understood. Additionally, aerosol coatings and their capacity to shield pollutants from degradation is a recent discovery, but important to estimate atmospheric PAH concentrations, of not only LMW PAHs but also their heavy relatives.

e. Sources

The lion's share of PAHs in the environment originates from human activities. (Callén et al. 2008) Naturally, higher concentrations of PAHs are found in vicinity to emission sources – therefore conurbations. (Keyte et al. 2013) However, also natural sources are known for various PAHs. (Cabrerizo et al. 2011) Generally speaking though, PAHs are the product of incomplete combustion processes, wherein the substrate and its moisture content, the combustion temperature and the availability of oxygen play a major role for formation processes of PAHs in terms of PAH profile as well as the total amount formed in the process. (Lu et al. 2009; MASTRAL et al. 1999; Mastral et al. 1996)

Anthropogenic sources include coal and coke production, wood or peat burning, petrol, diesel and oil combustion as well as industrial processes such as chemical manufacturing. They also arise as byproducts at gasworks or creosote manufacturing. (Mostert et al. 2010; Cao et al. 2019; Collins et al. 1998; Lundstedt et al. 2007)

Additionally, the anthropogenic realm can be further subdivided into pyro- and petrogenic- sources, wherein the petrogenic sources include all fossil fuel-based combustion processes while the pyrogenic sources comprise biomass burning. Analytically it is very well possible to differentiate in between the two origin groups by looking into alkylation efficiency patterns of low molecular mass PAHs, wherein the alkylation patterns allow to determine the origin. (Hindersmann Ben and Achten 2011)

Natural sources likewise include biomass burning but also volcanic eruptions, diagenesis, (Wang et al. 2007) and biological activity of e.g. fungi, insects, marine organisms and soil microbial activity.

Perylene for one is believed to be the product of fungal, insectile or marine organisms. (Cabrerizo et al. 2011) Some sources provided results describing the production of Phenanthrene and Naphthalene in remote soils and sediments. (Wickstrom and Tolonen 1987; Laflamme and Hites 1978) and others have found significant amounts of Phenanthrene, Naphthalene and Perylene in termite nests, wood and soils of tropical regions, suggesting the bioproduction of these compounds by termites. (Wilcke et al. 2000)

However, as implied before, these are all minor sources compared to anthropogenic activities, wherein motor exhausts, coal-related domestic heating and industrial processes are thought to be the dominant sources of PAHs in the atmosphere on a global scale. (Wang et al. 2007) Yet, dominant sources might vary locally. Zhang et al. 2009 reported that in China 47% of PAH emissions are based on biomass burning, 39% in small-scale coke production and only 8,3% on domestic coal combustion while 3,9% are due to industrial processes respectively. As the biggest emitting countries of the 16 EPA PAHs, the paper names China (114 kt/year), India (90 kt/year) and the USA (32 kt/year). (Zhang et al. 2009)

Interestingly, there are a few PAHs that are used to identify different PAH sources. Typical fire markers for instance, are Fluoranthene, Pyrene, Benzo(a)anthracene, Dibenzo(a,h)anthracene, and Indeno(1,2,3-cd)perylene. Coronene – a non-EPA PAH – is often used as a marker for motor vehicles, particularly gasoline fueled ones. (Freeman and Cattell 1990) Other researchers suggested to look at PAH ratios to identify sources. Table 4 displays different PAH ratios in gaseous and particulate phases as well as total PAH ratios and suggests an origin based on them. The values were extracted from (Lai et al. 2011), whereas the authors derived these ratios and compared them to results of other studies. Some isomer ratios are used extensively to determine emission origins of PAHs.

Type of sample	$\frac{B(a)A}{(B(a)A + Chr)}$	$\frac{FluA}{(FluA + Pyr)}$	$\frac{I(1,2,3-c,d)P}{(I(1,2,3-c,d)P + B(ghi)P)}$	$\frac{B(a)P}{(B(a)P + Chr)}$	$\frac{I(1,2,3-c,d)P}{B(ghi)P}$	$\frac{B(a)P}{B(ghi)P}$
Gaseous						
AVE	0,16 ± 0,09	0,57 ± 0,08	-	-	-	-
Range	0,06 – 0,47	0,39 – 0,78	-	-	-	-
Particulate						
AVE	0,33 ± 0,06	0,5 ± 0,09	0,52 ± 0,03	0,49 ± 0,08	1,07 ± 0,13	0,61 ± 0,44
Range	0,21 – 0,45	0,13 – 0,59	0,42 – 0,57	0,35 – 0,76	0,72 – 1,31	0,34 – 2,75
t-PAHs						
AVE	0,26 ± 0,08	0,57 ± 0,07	0,52 ± 0,03	0,26 ± 0,14	1,38 ± 1,43	1,09 ± 0,11
Range	0,14 – 0,52	0,39 – 0,69	0,42 – 0,57	0 – 0,48	0,4 – 6,55	0,87 – 1,3
Origin	Petroleum/Vehicle	Coal/Wood	Vehicle coal/wood	Diesel	Diesel	Traffic emissions/Others

Table 4: PAH ratios of gaseous, particulate as well as total PAHs (t-PAHs) and their suspected sources of origin

Though, it is important to consider the reactivity and the photochemical degradation rate – and therefore the geographic and climatic conditions - of the selected PAH and its location of origin (which, as discussed in the chapter “3d properties of PAHs”, is not entirely easy) because that may alter the overall distribution of the compound investigated and subsequently the result. (Lai et al. 2011)

Figure 3 shows the results of different burning profiles from a study by (Freeman and Cattell 1990). As indicated before, different substrates do show different PAH profiles. The figure differentiates in between domestic open wood, Australian wood, open barbecue cooking of meat with Australian

wood, large scale backyard burn of native and introduced species, some cardboard products, large scale bushfires – consuming only native species, leaves from native vegetation burnt on open fire and commercial incinerator burning paper and cardboard products profiles were compared to each other. Note, that the profile refers to gas emissions and not to combustion remains, such as ash, charcoal or soot. The profiles of the remains as well as the profiles of gas and particulate phases would be quite different. Also, only a few PAHs have been investigated in this study, while in reality the PAH profile would contain many more compounds.

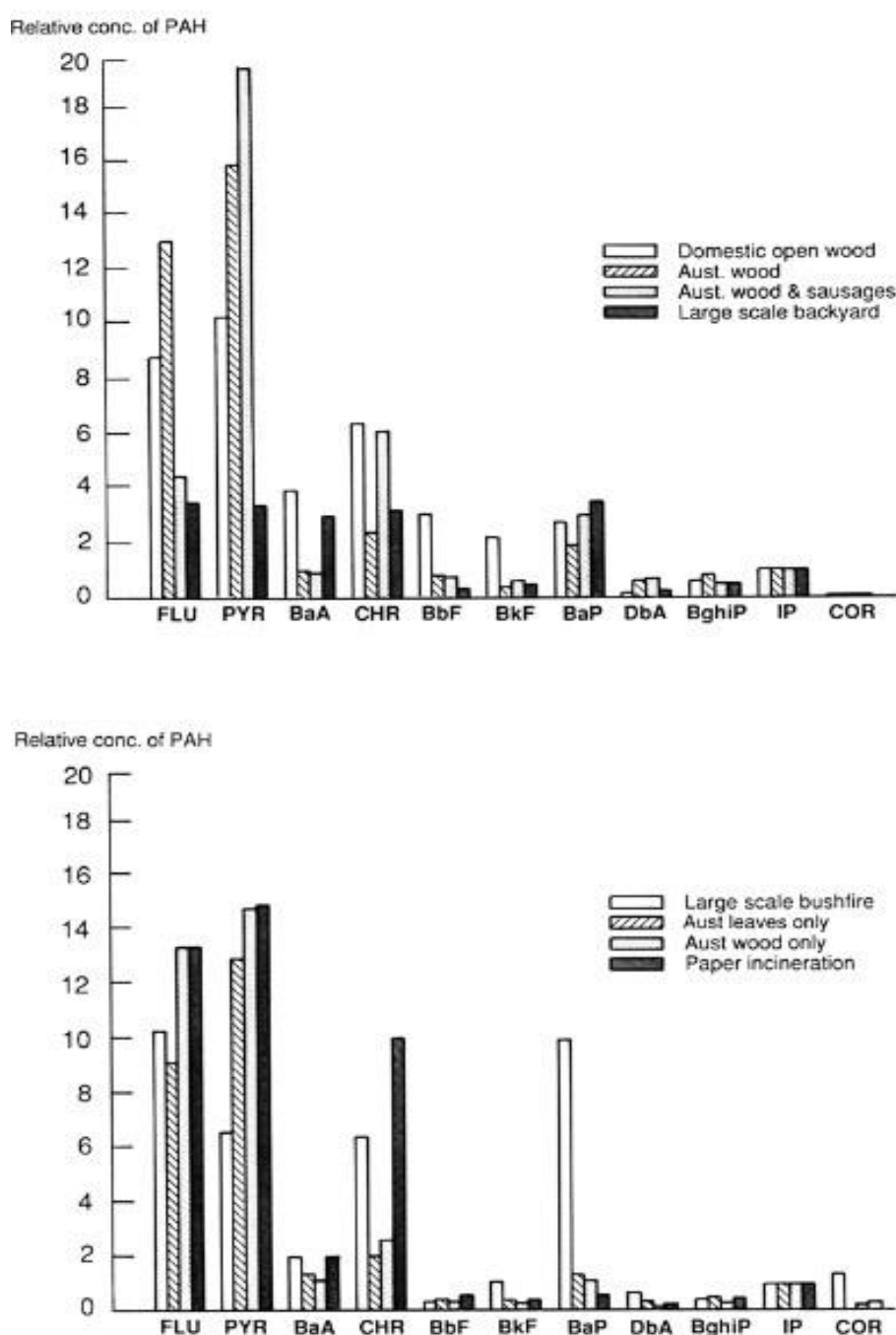


Figure 3: Profile of PAHs from the burning of wood and other vegetation; (Freeman und Cattell 1990)

Another study by Samburova et al. in 2016 investigated the emission profiles of 5 different biomass fuels, namely: Siberian peat, Alaskan peat, Florida swamp peat, ponderosa pine needles and

cheatgrass. The PAH contents of the particulate phases were compared to the contents in vapor phases. While considering 133 different compounds, the ten most abundant PAH(-derivates) were used for comparison purposes. Only four particulate PAHs and three in the vapor phase are part of the 16 US-EPA priority PAHs and none of them were listed as “most abundant” for both phases. That does not mean, they’re not found as gas as well as particulates. Yet, it means that they do not constitute the 10 most abundant compounds in both phases. The profiles created allow a direct comparison of the substrates and show distinct patterns for all of them. Even the three peat-based materials showed very distinct profiles as they are all based on different biomass mixtures constituting the peat. Additionally, an abundancy analysis of two, three, four, five and six ring PAHs in the particulate and gas phases was conducted. Interestingly, the particulate phases held a considerable amount of low molecular weight PAHs, wherein at least half of PAHs found, were based on 2 and 3 ring structures. Vapor phase PAHs were almost exclusively two ring structures with some contribution of three ring PAHs for peat based fuel materials. (Samburova et al. 2016)

Numerous studies have been conducted on PAH profiles of different substrates. (McGrath et al. 2001) compared the profiles of cellulose and pectin in 2001, (Karavalakis et al. 2011) conducted a study on biodiesel emission profiles of not only but also PAHs in 2011, (Atkins et al. 2010) investigated the constitution of PAH emissions from different biomass pellets in wood fired combustion boilers and different flame operating modes, just to name a few. All of them show different PAH profiles, mostly depending on the substrate.

As mentioned previously, other factors such as the availability of oxygen, the moisture content and the combustion temperature also have major influencing capacities on PAH formation. However, the characteristics of these capacities seem to divide the scientific community. Various studies published results, that found a rise in PAH formation with rising temperature, (Ledesma Elmer B. 2002; McGrath et al. 2001; Gulyurtlu et al. 2003; Sánchez et al. 2013; Lu et al. 2009) while other papers reported contrary results, wherein the formation of PAHs decreased with temperature combined with a formation maximum at around 400 to 500°C. (Brown et al. 2006; Devi and Saroha 2015; Hale et al. 2012; Keiluweit et al. 2012)

The most striking difference in between the two opposite causal relationships seems to be the substrate. The authors that reported an increase in PAH formation with higher temperatures investigated biomass combustion, (e.g. rice & bean straws, coconut shells, soot or catechol) while the authors that published papers on the decrease of PAHs with increasing temperatures investigated solely (bio)chars.

According to (Izaurrealde et al. 2012) biochar is the product of low temperature heating of plant residues or other lignocellulosic organic materials in presence of low O₂ concentrations (=pyrolysis). Because of that the PAH content in biochar may be depending on the degree of pyrolysis, since prior volatilization of PAHs might have occurred during pyrolysis.

A study by (Weidemann et al. 2018) compared PAH concentrations in different biochars and their substrates at three different pyrolysis stages. The maximum temperatures decreased, and carrier gas flows increased from stage I to stage III and heating types as well as operation modes varied from one stage to another. Softwood, wheat straw and anaerobic digestate were used as substrates.

The results revealed, that for wheat straw the PAH content is very much depending on pyrolysis stages, whereas the highest concentrations occurred at 550°C and stage III (20 µg/g biochar), followed by stage II with 12 µg/g biochar and stage I with 6 µg/g biochar. The response of softwood did not display

much of a variation. At 700°C a small difference of 1 µg/g biochar in between the three stages was visible. The study also evaluated the ring structure size of the produced PAHs. The lion's share of all PAHs formed (>85%) for all substrates, pyrolysis stages and temperatures were low molecular weight PAHs (LMW PAHs = 2 or 3 benzene rings)

As previously mentioned, the combustion temperature, the oxygen content and the moisture content of the substrate have major influencing capacities on PAH formation. A study by (Lu et al. 2009) investigated these capacities for two different substrate types, namely: rice straw and bean straw. While doing so, the authors further investigated these capacities on PAH emissions and the PAH content in residues. Burning temperatures reached from 200 to 700°C.

They found that temperature variation had little effect on PAH contents in residues, whereas contents of both substrates were found below 0,1 µg/g for the whole temperature spectrum investigated. The emissions on the other hand showed a very strong response to increasing temperatures. Rice straw emissions ranged from 9 µg/g at 200°C to 24 µg/g at 700°C and displayed a rather continuous rise of emissions with temperature. Bean straw emissions ranged from 4 µg/g at 200°C to 50 µg/g at 700°C and displayed an e-function like increase with temperature, whereas emissions stayed rather constant below 400°C and displayed a sharp rise thereafter.

Additionally, one must say that at a certain point with increasing temperature the PAH formation process will be superseded by thermal decomposition. However, the threshold temperatures reported are somewhere in the range of 750 to 1050°C respectively. (Lu et al. 2009; Ledesma Elmer B. 2002; Sánchez et al. 2013; Gulyurtlu et al. 2003)

The influence of moisture content of the substrate was also investigated by the same study (Lu et al. 2009) while burning the materials at 700°C because of the PAH formation maximum at that temperature. Apparently, the moisture content had an unfavorable effect on PAH emissions, wherein a higher content lead to decreased PAH emissions. A moisture content of 30% lead to an emission decrease by 78% for bean straw at in relation to dried straw (0% moisture content), whereas the moisture content had a stronger effect on LMW PAH decrease. It is assumed that the water content induces PAH destruction by forming hydroxyl radicals that enhance PAH degradation. This will be explained in greater detail further along this thesis in the chapter *"3g Degradation, the role of vegetation, remediation and sinks"*. (Mcdow et al. 1995)

The oxygen content, given by the authors in percent, showed a behavior similar to a gaussian distribution regarding PAH formation, whereas the peak was found at an oxygen content of 40%. It is generally accepted, that the influence of O₂ contents and the proper mixing with burning materials are essential for complete combustion processes. (KILGROE et al. 1990)

Therefore, the amount of PAH formed during a combustion process is supposed to decrease with rising oxygen content and resulting combustion progress. (Umweltbundesamt 2016; Sánchez et al. 2013) This circumstance is true for high temperatures and low oxygen contents.

A study by Sánchez et al. 2013, investigated the PAH and soot formation for oxygen contents of 1, 2, 3, 4 and 5 volume percent respectively. It investigated soot formation from acetylene conversion at a concentration of 30 000 ppmv (3 volume percent). The response to low oxygen contents was significant for high temperatures (950°C) displaying a considerable increase of PAH as well as soot formation with lower oxygen concentrations, whereas little response of PAH and soot formation was observed at a temperature as low as 700°C. (Sánchez et al. 2013) These results align with other studies

such as You et al. 1994, which also reviewed PAH formation under low oxygen concentrations (You et al. 1994) or (MASCLET et al. 1987).

However, the presented study by (Lu et al. 2009) investigated the phenomenon concerning higher oxygen concentrations. In fact, so high, that these results are not of environmental concern, since they largely exceed commonly found oxygen contents.

Another factor influencing PAH formation, is the duration of the combustion process. Because PAH formation is the result of incomplete combustion, shorter combustion durations equal less combustion and concomitantly higher PAH formation. (Hale et al. 2012)

f. Toxicity

As addressed in the introduction, PAHs are known to have carcinogenic, teratogenic and mutagenic effects on the human organism, (Cao et al. 2019) additionally they are considered toxic to all living organisms, (Tobiszewski and Namieśnik 2012) and therefore also possess ecotoxicological features. (Sverdrup et al. 2002)

PAHs are known to be toxic to animals as well as biota in soils and aquatic ecosystems. (Bispo et al. 1999) In fact, knowledge about the harmful effects in animals is more extensive than the knowledge regarding humans. Several papers have already been published in the 80s regarding adverse effects caused by PAHs observed in mice. (Collins et al. 1998) listed some of these effects as: *“impacts on the reproductive system, cardiovascular toxicity, bone marrow toxicity, immune system suppression and liver toxicity”*, while quoting (MacKenzie and Angevine 1981; Paigen et al. 1985; Legraverend et al. 1983; Hardin et al. 1992) and (Hardin et al. 1992) as sources (p. 1). Additionally a large number of PAHs, including their derivatives, are known to have mutagenic and genotoxic features. (Collins et al. 1998)

In the human organism PAHs are known to cause bronchitis, respiratory as well as pulmonary problems when inhaled and skin-, lung- and stomach- cancer when exposed at various exposure pathways.

The efficacy of the individual PAH cocktail strongly depends on the exposure pathway as well as the constitution of the mixture itself. (Schneider et al. 2002; Tsapakis and Stephanou 2005)

For inhalative exposure, suitable cancer potency estimates have been derived from epidemiological data by the WHO as well as the German ministry of environment. (Schneider et al. 2002)

Dermal exposure to PAHs is nowadays mostly a problem for workers employed in high risk environments. Studies have found elevated levels of PAHs in urine samples of creosote workers, (Elovaara et al. 1995) and coke oven workers (VanRooij et al. 1993a) and aluminum workers (VanRooij et al. 1993b). (VanRooij et al. 1993b) explained that dermal uptake is mostly based on depositions from air or contact with contaminated surfaces like clothing or tools. Anatomical site-specific skin adsorption rates can be evaluated and compared to metabolites in urine samples of e.g. 1-Hydroxyl-Pyrene whereas excretion rates are derived for evaluation.

Studies on oral carcinogenic effects are much easier to conduct compared to inhalative or dermal exposure but require longer time periods because of the strong time dependency of responses. Since regulation is often based on B(a)P as indicator substance, these studies have been mostly carried out with pure B(a)P and complex PAH mixtures e.g. coal tars in comparison to B(a)P. (Culp et al. 1998; Weyand et al. 1995)

Regarding risk assessment, German regulations rely on B(a)P thresholds, wherein the soil content must not exceed certain trigger values. According to a decree passed in 1999 by the ministry of justice and customer protection, these threshold values were initially set to be at 2 mg/kg soil for playgrounds, 4 mg/kg soil in residential areas, 10 mg/kg soil in parks and recreational green spaces and 12 mg/kg soil in industrial areas. (Bundesministerium der Justiz und für Verbraucherschutz 7/12/1999)

Currently, an amendment of this law is drafted, which includes a reduction of these values to 0,5 mg/kg in playgrounds, 1 mg/kg in residential areas or parks/recreational areas and 5 mg/kg in industrial areas, is being negotiated between committees, federations and states in Germany. (Bundesrat 566/17 2017) Formally all states and institutions agree on this reduction, yet they discuss the details of this amendment as it does not only evolve around PAHs.

If these trigger values are exceeded B(a)P -equivalents are evaluated as indicated in table 5. The values were extracted from a decree released by the ministry of energy, agriculture, environment and rural regions in 2017. (MLUR 2017)

	Acy	Anth	FluA	BaA	Chr	B(b)F	B(k)F	B(a)P	B(ghi)P	I(1,2,3)P	DB(a,h)A	Sum of toxicological equivalents
TEF	0,01	0,01	0,01	0,1	0,01	1	0,1	1	0,01	0,1	1	
Soil content	<0,05	0,9	3	1,7	1,8	1,7	0,8	1,6	0,9	0,7	0,12	
Toxic equivalents	-	0,009	0,03	0,17	0,018	1,7	0,08	1,6	0,009	0,07	0,12	3,8
Share of sum	-	0,2%	0,8%	4,5%	0,5%	45%	2,1%	42%	0,2%	1,8%	3,2%	

Table 5: Evaluation of toxicological equivalents using TEFs and concentrations in soil. (MLUR 2017)

In a nutshell: The TEF value is multiplied with the corresponding concentration (soil content), which gives the toxicological equivalent. When this is done for all PAHs, the toxicological equivalents can be summed up and constitute, combined, the sum of toxicological equivalents. This combined value is then used to determine if the threshold is exceeded or not.

The so called TEF-approach (Toxicological equivalency Factor) is built upon several assumptions, (Nisbet and LaGoy 1992) listed four of them in a paper published in 1992 page 2:

1. "A reasonably well-characterized compound can be selected to serve as surrogate or reference compound for all members of the class."
2. "The toxic effects of all members of the class are qualitatively similar to those of the surrogate compound and may be characterized quantitatively by means of a relative potency or TEF."
3. "TEFs for different toxic end points are similar, so that limited information on relative toxic potencies in one or a few assay systems can be used to assign TEFs to single compounds or subclasses for other end points"
4. "The toxic effects of different compounds of the mixtures are additive."

Additionally, German officials stipulated that B(a)P must hold a share of total toxicity in the range of 30 to 60% and that the other 15 EPA – PAHs must not exceed a defined ratio to B(a)P (figure 4), for the legislation to apply, if the thresholds are exceeded. (MLUR 2017)

Naph	160	BaA	6
Acy	5	Chry	5
Ace	95	BbF	3
Flu	110	BkF	3
Phen	140	BaP	1
Anth	240	BghiP	3
FluA	55	I123P	3
Pyr	30	DBahA	1,5

Figure 4: Shares that must not be exceeded as determined by German legislation. (MLUR 2017)

$$\frac{[Single\ PAH]}{[BaP]} \neq > \text{value indicated in figure 21}$$

As indicated in the previous paragraph, PAHs were appointed toxicological equivalents to simplify the toxicological evaluation process. Yet, only 11 of the 16 EPA PAHs were appointed TEF-values by German officials, wherein the other 5 are regarded as if their toxicological equivalent was zero. These 5, namely Naphthalene, Acenaphthene, Fluorene, Phenanthrene and Pyrene are assumed to have little to no toxicological features – as the value

zero suggests. That is not to say, that there is no toxicological activity to be expected.

(Nisbet and LaGoy 1992) were the first ones to have assigned values of 0,001 to these 5 compounds, arguing that they make toxicological evaluations using the TEF approach more precise and that the appointment of TEFs to slightly toxic compounds is generally harder but necessary since toxicological effects are to be expected.

Compound	Abbreviation	TEFs by German Legislation	TEFs by Nisbet and LaGoy 1992	TEFs used for toxicity evaluation
Benz(a)anthracene	B(a)A	0,1	1	0,1
Benzo(a)pyrene	B(a)P	1	1	1
Dibenz(a,h)anthracene	D(a,h)A	1	0,1	1
Benzo(b)fluoranthene	B(b)F	1	0,1	1
Benzo(k)fluoranthene	B(k)F	0,1	0,1	0,1
Indeno(1,2,3-c,d)pyrene	I(c,d)P	0,1	0,1	0,1
Chrysene	Chry	0,01	0,01	0,01
Anthracene	Anth	0,01	0,01	0,01
Benzo(g,h,i)perylene	B(ghi)P	0,01	0,01	0,01
Fluoranthene	FlA	0,01	0,001	0,01
Acenaphthylene	Acy	0,01	0,001	0,01
Phenanthrene	Phen	-	0,001	0,001
Pyrene	Pyr	-	0,001	0,001
Fluorene	Flu	-	0,001	0,001
Acenaphthene	Ace	-	0,001	0,001
Naphthalene	Naph	-	0,001	0,001

Table 6: TEFs assigned to the 16 EPA PAHs by German Legislation and Nisbet and LaGoy 1992

Table 6 displays TEF values as given by Nisbet and LaGoy in 1992 and by German officials in 2017. Similar TEFs are highlighted in light green, while contrary TEFs are highlighted in light red. (Nisbet and LaGoy 1992; MLUR 2017) As one can conclude, assigning and evaluating toxicological features using the surrogate marker approach is no precise nor unambiguous endeavor.

However, the approach does not serve to determine toxicological features of a sample per se but serves to reveal possible contaminated sites and identify threshold exceedings, as given by German officials. Wherein, the threshold values are set to absolutely fall below effect dosages on which they rely upon. Therefore, this approach allows to ignore several effects of antagonistic and synergistic

nature and to determine if measures, such as remediation or use restrictions, are required to ensure public safety. As best understood antagonistic effect, sorption can be named. Sorbed contaminants are known to be almost non bioavailable and therefore dermal uptake is close to inhibited. (Weissenfels et al. 1992)

The synergistic effects on the other hand are not as well understood. As indicated before, for the surrogate marker approach to hold, the same physiological end point must be affected and the toxic effects of mixtures must act additive. (Nisbet and LaGoy 1992)

Because of the considerable health concerns regarding PAHs, many studies have been conducted that explored the nature of B(a)P as well as PAH mixture toxicity. Table 7 was extracted from (Schneider et al. 2002) wherein the authors intended to demonstrate the gap between observed adverse effects and mathematically assessed potency ratios using the B(a)P approach as well as the total amount of PAHs. The left-hand side compares calculated toxic potency of B(a)P equivalents to the observed potency by dermal or oral ingestion and demonstrates that PAH mixtures are often several times more toxic than what would be mathematically expected. The right hand side displays the gap in between the calculated potency of the mixture divided by the potency of B(a)P $\frac{[Mixture]Potency}{[B(a)P]Potency}$, often displaying two digit results. Except for a regular pattern that can be observed in both graphs, regarding forestomach tumors by ingestion of mice, results show significant disparities.

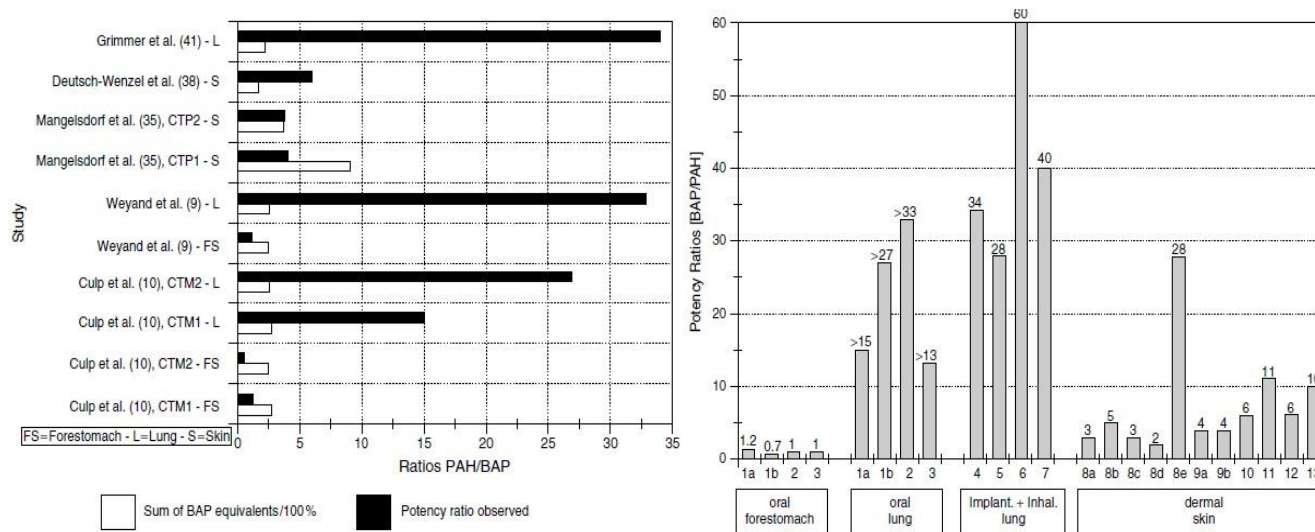


Table 7: Left: Potency ratios of B(a)P and the sum PAH based on predictions of relative potency values (B(a)P equivalents). Right: Potency ratios btw. B(a)P and the sum PAH (potency of mixture divided by potency of B(a)P). (Schneider et al. 2002)

As striking as these results are, it is important to add that the PAH sources within these studies were based on coal and roofing tar mixtures, manufactured gas plant residues, automobile exhaust condensates and extracts as well as flue gas condensates. Because of that, one might argue that these sources and their profiles do not represent background values of natural soils as this is what the surrogate marker approach is used for in Germany.

However, nowadays roughly half of the PAHs ingested by humans in Germany is based on dietary intake. (Dr. Andreas Zeddel 4/27/2017) Some edible plants like lettuce, potato and carrot are known to transfer PAHs to their edible parts (Fimes et al. 2002) and others, such as grapes, apples, pears,

tomatoes, cabbage, lettuce, cereals, oils and fats, smoked fish and meat, coffee as well as tea have been found to contain elevated levels of PAHs on their surfaces. (Rojo Camargo et al. 2011; Paraíba et al. 2011) Particularly processed foods raised concerns of international safety organizations, such as the SCF, FAO and EFSA. (SCF 2002; EFSA 2008)

In order to verify the validity of the B(a)P -approach as reference substance for the total concentration of PAHs in food, the European commission argued that the monitoring of these 15+1 compounds in regards to long-term exposure assessments is necessary. (SCF 2002; Simon et al. 2007)

Compound	Abbreviation	PAH2	PAH4	PAH8
Benzo(a)pyrene	B(a)P	✓	✓	✓
Chrysene	Chry	✓	✓	✓
Benz(a)anthracene	B(a)A		✓	✓
Benzo(b)fluoranthene	B(b)F		✓	✓
Benzo(k)fluoranthene	B(k)F			✓
Indeno(1,2,3-c,d)pyrene	I(c,d)P			✓
Dibenz(a,h)anthracene	D(a,h)A			✓
Benzo(g,h,i)perylene	B(ghi)P			✓

Table 8: PAH2, PAH4 and PAH8 as defined by the EFSA

In 2008 the EFSA's Panel on Contaminants in the Food Chain (CONTAM) published a report presenting their results on the toxicological evaluation of PAH mixtures in food. Within this report the toxicity of solely B(a)P, as well as more compounds, namely Benzo(a)pyrene, Chrysene, Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-c,d)pyrene, Dibenz(a,h)anthracene and Benzo(g,h,i)- perylene or in short: PAH2, PAH4 and PAH8 were compared – Table 8.

According to the results by the (EFSA 2008), the evaluation based on solely B(a)P as well as PAH2 were insufficient. Furthermore, the journal explained that PAH4 and PAH8 on the other hand posed a more accurate representation of the toxicological reality and reasoned their argument with numbers: *"The correlation between PAH2 and PAH4 or PAH8 was determined to be at 0,92 and between PAH4 and PAH8 at 0,99. Of samples negative for PAH2, 26% and 18% identified concentrations above the LOD for at least one other PAH for samples tested for all PAH15 or all PAH8, respectively."* (p. 3) (EFSA 2008) Based on these results, the regulations on PAH assessment in food were amended by adding respective maximum concentrations for Benzo(a)pyrene and the sum of PAH4 in food, namely: Benzo(a)pyrene, Chrysene, Benzo(a)anthracene and Benzo(b)fluoranthene, in 2011. (EU comission No 835/ 2011; Schulz et al. 2014; EFSA 2008)

In short: Determining toxicological potencies in equivalents, as introduced in this chapter, is used as shortcut to evaluate possible health risks for humans, regarding soils they are in contact with. This shortcut involves prerequisites that must be met in order for this approach to apply, namely: the toxicological share of B(a)P must be between 30 and 60%, shares of other PAHs compared to B(a)P must be in a certain range and of course toxicological equivalence factors must be known. In the case of Germany, 5 TEFs are missing.

Even so, many studies have shown divergence between observed adverse effects of PAH mixtures and calculated potencies (Schneider et al. 2002), which is why an alternative approach was suggested by the EFSA in 2008, wherein not only B(a)P is used for evaluation.

g. Degradation, the role of vegetation, sinks and remediation

Vegetation has the capacity to function as “filter” for airborne PAHs, wherein tree, shrub, herb and woodland vegetation covers trap airborne PAHs and subsequently accumulate PAHs in soil. This phenomenon is called “*Forest Filter Effect*” and is based on the vertical profile of the vegetation cover. The high vertical profile of shrub, herb and woodland offers more surface to capture airborne PAHs than grassland, while the deposition in grassland is based entirely on direct deposition. In other words: Larger canopies and diversified species composition enhance interception of airborne PAHs. (Peng et al. 2012) This filter effect for semi-volatile organic compounds (SVOCs) is noticeably stronger for hydrophobic compounds with higher LogK_{OW} and LogK_{AW} values and has been found to also depend on the surface properties of plants, such as orientation, roughness, hairiness, petiole length, rigidity and wettability. (Peng et al. 2012; Terzaghi et al. 2013; Maddalena et al. 2003) Because of the plant as well as contaminant property dependency on the adsorption processes, different PAH profiles can be observed for distinct plants. (Howsam et al. 2000) When PAHs are sorbed to foliage surfaces, they can be degraded through solar radiation (photodegradation) and microbial conversion (biodegradation) or reduced via revolatilization, wash-off and wind blow. (Nadal et al. 2006)

Some edible plants have been found to transfer PAHs to their edible parts or to contain elevated levels of PAHs on their surfaces. (Rojo Camargo et al. 2011; Paraíba et al. 2011) The waxy surfaces of these plants are able to adsorb low molecular PAHs or take them up through stomata, which were possibly re-volatilized. The heavier representatives of the class (HMW PAHs) may pollute the surface due to atmospheric deposition. (EFSA 2008; Meudec et al. 2006)

Some plants are known to extract persistent PAHs from soils, while in turn others have no or even inhibitory effects due to enhanced holding capacities of roots in the rhizosphere, (Liste and Alexander 2000) and some are believed to enhance microbial degradation processes using C-exudates that support microbial communities. (Reilley et al. 1996) Because of these mechanisms, plants can be used for In-Situ PAH remediation.

Bioremediation systems generally consist out of at least four different pathways to reduce bioavailable contaminant levels. Abiotic losses (e.g. leachate, volatilization, phytodegradation, irreversible sorption, chemical degradation, indigenous microbial degradation, root tissue enhanced dissipation and root-exudate enhanced biodegradation. (Sun et al. 2010)

In turn, contaminants in soils (including PAHs) can be grouped into four fractions regarding their chemical and biological availability. A “lost fraction” or “labile fraction” that is based on initial contaminant decrease by processes such as leaching, volatilization, photolysis and/or biodegradation. Initially applied PAHs to soil experience a relatively rapid loss, whereas this fraction’s concentration decreases over time. Also, with time, depending on the compound and the soil properties, a process known as aging takes over. This phenomenon describes how the associations in between PAHs and soil particles become stronger, resulting in unavailability of contaminants for microorganisms. This is why the fraction is also called “Non-extractable fraction” and its concentration increases over time.

The two remaining PAH fractions can then be divided into two groups: a fraction that is available chemically as well as biologically, also called “available fraction” which decreases over time (due to aging) and a strongly bound “non-recalcitrant fraction” which is harshly extractable from soil and also increases over time. The latter fraction is often believed to be “non-bioavailable”, however some

microbes were found to be able to access these compounds. (Stokes et al. 2005) The afore mentioned processes, namely indigenous microbial degradation, root tissue enhanced dissipation and the root-exudate enhanced biodegradation can therefore affect the available as well as the recalcitrant fraction of PAHs.

The tendencies for abiotic losses have been discussed within the chapter “3d properties of PAHs” and can contribute significantly to concentration reductions for low molecular weight PAHs due to their comparatively high-water solubilities and vapor pressures. A study by (Wild and Jones 1993) investigated abiotic losses of 4 different soils.

Three soils were spiked with sewage sludge that contained PAHs and one was left untreated as reference. Those 4 soils, namely AS1 rural agricultural soil with no previous sludge application, AS2 rural agricultural soils, FS rural coniferous forest soil and RS roadside demonstrate that loss rates for low molecular weight PAHs are much higher than for high molecular weight PAHs. In all four spiked soils >75% of Naphthalene was lost, other LMW PAHs were found to be lost between 0 and 77% (depending on soil type), whereas the numbers for HMW PAHs of 0 to 13% suggest that this phenomenon is of less relevance for these compounds.

The remediation process can also rely on indigenous bacteria, wherein the degradation capacities might be stimulated in situ. While low molecular mass PAHs, composed of two or three benzene rings, are easily degraded through biological processes, high molecular weight PAHs with more than four rings are more resistant to microbial degradation. This is due to their properties, high molecular PAHs partition into clay and organic matter which renders these compounds less bioavailable. Nonetheless, biodegradation is a promising, low-cost alternative to chemical degradation processes. (Sun et al. 2010)

It can occur under various chemical conditions (aerobically, anoxically or anaerobically) in all media as well as across media (soil, air and water) and with different electron acceptors (nitrogen, oxygen, sulfur and sometimes $\text{Fe}^{(\text{III})}$ and $\text{Mn}^{(\text{IV})}$). An extensive number of studies have been published on the biodegradation capacities of bacteria, ligninolytic and non-ligninolytic fungi, archaea as well as microalgae (cyanobacteria, diatoms etc.) and various review papers have been published in the attempt to combine the knowledge held in those papers. (Ghosal et al. 2016; Lu et al. 2011; Mallick et al. 2011)

Various metabolic pathways of bacterial PAH degradation mechanisms have been documented, whereas it is possible to group them into two categories: aerobic processes with oxygen and anaerobic processes without oxygen. In aerobic degradation processes, oxygen does serve as co-substrate for the hydroxylation step and oxygenolytic ring cleavage of the ring systems and as final electron acceptor. In anaerobic processes the aromatic ring system is attacked with reductive reactions, wherein the exact mechanisms remain unclear. However, alternative compounds, such as nitrate (NO_3^-), sulfate (SO_4^{2-}), iron^(III) (e.g. $\text{Fe}(\text{OH})_3$) or manganese^(IV) (e.g. MnO_2) serve as final electron acceptors. (Ghosal et al. 2016)

Under anaerobic conditions (e.g. in aquifers, aquatic sediments or submerged soils) nitrate-based remediation techniques are used extensively because of the high solubility of nitrate (10 000x higher than oxygen – if the electron accepting efficiency is considered) and its ability to yield approximately the same amount of energy as under aerobic conditions. Additionally, nitrate compounds (e.g. $\text{Ca}(\text{NO}_3)_2$) are comparatively cheap and easy to obtain. Large scale aerobic bioremediation techniques on the other hand are often regarded as critical, because of their limitations in terms of oxygen-supply

and the costly technical realization of such methods regarding aquatic sediments. Furthermore, complications regarding application might lead to re-suspension of sediments and nutrients previously captured in them.

Sulfate-reducing conditions are mostly found in marine sediments, where oxygen as well as nitrogen is scarce, and sulfate is abundant. Yet, only in some cases iron and manganese reduction are the dominant process in marine sediments because bacteria has to deal with the low solubility of these metals at neutral pH values and their subsequent unavailability. (Lu et al. 2011)

Bioavailability in soils is often limited by the high hydrophobicity and strong sorption of high molecular weight PAHs. Biodegradability sinks accordingly with higher molecular mass and therefore higher toxic capacities of these compounds. This problem can be mitigated by using surfactant-based remediation techniques, wherein the surfactant settles on these hydrophobic PAHs, making them more soluble, subsequently more bioavailable and therefore better degradable. These technologies use different types of surfactants that can be grouped into synthetic- or biological- and ionic- (anionic and cationic) or non-ionic surfactants, also mixed types are available. Numerous studies have been published on the success of different methods, which again have been summed up in various review papers. (Lamichhane et al. 2017; Mao et al. 2015) Alternative remediation techniques include physical, chemical, thermal or biological remediation technology whereas chemical and biological remediation techniques will be discussed in greater detail later in this chapter.

Most fungi capable to degrade PAHs are not capable to use them as only energy source but may co-metabolize PAHs to numerous oxidized products and in sometimes also CO₂. Dioxygenase enzymes and monooxygenase mediated reactions is how bacteria and algae mainly degrade PAHs. Fungal degradation involves mostly monooxygenase mediated reactions. Yet, the degradation reactions usually involve several enzymatic pathways that depend on the species as well as growth conditions. In essence, there are two types of fungi, able to degrade PAHs: ligninolytic fungi or white-rot fungi (capable of producing peroxidases, including lignin and manganese peroxidase as well as laccase that allows them to degrade lignin in wood). Both enzymes and the phenol oxidase enzyme (laccase) hold the ability to oxidize PAHs. And second non-ligninolytic fungi (who instead produce Cytochrome P450). Compared to PAH degrading bacteria, they are not promoted when in contact with PAHs nor its degradation products. Non-ligninolytic fungi may not be able to produce peroxidases nor laccases but Cytochrome P450. Cytochrome P450 is a monooxygenase that catalyzes the ring epoxidation of PAHs to form unstable arene oxides which can then further degrade. (Ghosal et al. 2016)

So far little attention has been paid to microalgae. However, these organisms play an important role regarding the fate of PAHs in aquatic ecosystems and numerous strains are known to metabolite PAHs such as Naphthalene, Phenanthrene, Anthracene and Benzo(a)pyrene. Some even more than one at a time: *Skeletonema Costatum* and *Nitzschia sp.* are able to accumulate and degrade phenanthrene as well as fluoranthene at the same time. (Ghosal et al. 2016)

Metals have effects on biosorption and biodegradation processes in these ecosystems and even inhibitory effects on microbial growth and activity. Studies showed, that the exposure time to those metals had a significant effect on the ability of some algae to remove low molecular weight PAHs but showed no effects on the removal efficiency for high molecular PAHs. (Ke et al. 2010)

The effectiveness of microorganisms capable to bioremediate PAHs has mostly been studied under controlled (laboratory) conditions. That means: A next to neutral pH, standard temperature (25°C) and good nutrient as well as oxygen supply. At contaminated sites however, the conditions will deviate

from those conditions and must allow microbial growth as well as the expression of enzymatic activity, so that the remediation process can take place. Several biotic and abiotic factors will differ from site

PAH Biodegradation		
Soil properties	PAH Properties	Microbial Properties
Presence of alternative C-sources	Molecular Weight	Surfactant production
Nutrient content	Bioavailability	Substrate range
Porosity	Hydrophobicity	Species abundancy
Temperature	Water Solubility	Metabolic pathways
Soil-PAH contact time (aging)	Concentration	Substrate affinity
pH	Structure	Diversity
Mass transfer		Prior exposure
Organic matter content		

Table 9: Factors that influence the biodegradation process, as explained by (Ghosal et al. 2016)

to site and may enhance or inhibit microbial activity and therefore the biodegradation process.

Table 9 lists a few factors that influence the biodegradation process of PAHs. (Ghosal et al. 2016) Temperature for instance has a powerful effect on the process, because obviously the site will not display the optimal temperature, nor will it be static year-round. During warm summer months, when temperatures rise, PAH solubility will increase which concomitantly increases bioavailability. However, oxygen solubility and therefore content will decrease along with the rising temperatures, this in turn reduces metabolic activities of aerobic microorganisms. Yet, some microorganisms named psychrophiles are capable of operating at low temperatures and act in contrast to thermophiles, who favor high temperatures. (Ghosal et al. 2016) In most studies, biodegradation has been examined under moderate temperatures. A few have been conducted under extreme temperatures. For instance (Brakstad and Bonaunet 2006) investigated biodegradation processes of hydrocarbons, which includes PAHs, at low temperatures in seawater (0° – 5°C).

Most Microorganisms are pH sensitive and favor next to neutral pHs. Yet, at contaminated sites the pHs are often far from neutral. Abandoned gasworks for example, often accommodate a lot of demolition waste such as concrete or brick and leach those substances into the surrounding soil increasing the pH value in the process. Leaching of coal spoils on the other hand, can generate acidic environments. (Ghosal et al. 2016)

Aerobic biodegradation processes depend upon oxygen for the oxygenase enzymes to be active. That is why oxygen may be a limiting factor for PAH degradation processes. Sometimes, that may require oxygen addition for aerobic in-situ degradation projects. These external sources include drainage or tillage techniques, added also chemicals that release oxygen, such as magnesium peroxide (MgO₂) can be used. (Ghosal et al. 2016)

Microbial activity is at its optimum when a certain nutrient level, usually in a certain composition regarding carbon, nitrogen, phosphorous and potassium, is guaranteed. However, at contaminated sites where the carbon content is high, and the nitrogen & phosphorous levels deplete rapidly. Nutrient levels are often insufficient and external supplements become necessary to enhance the biodegradation process. Yet, a surplus of nutrients may also lead to a decrease in microbial activity. (Ghosal et al. 2016)

In that sense, co-substrates are also known to limit the biodegradation process if insufficiently present. Substances like acetate (0,5-0.86 g/l), lactate (0,5-1,46 g/l), pyruvate (0,5-1,74 g/l), humic acid (5 g/l or 3,36-10,08 g/kg soil), cellulose (9,6*10⁻⁴-10 g/l) and sugars (glucose, sucrose) as well as alcohols

(methanol, ethanol) may play an important role in the degradation process. Because of its capacity to enhance the degradation process, it can additionally shift the carbon to nitrogen-ratio, aid microbial growth and benefit the activity of enzymes participating in the PAH degradation process. However, some researchers reported adverse effects from co-substrate addition due to competing activity in between the co-substrate and the substrate. (e.g. cellulose (Quantin et al. 2005)) and sometimes the addition of co-substrates might not have any effect at all. (Lu et al. 2011)

Even though bioremediation is an accepted cost-effective removal process regarding PAHs, it is difficult to generate sufficient microbial populations with satisfactory degrading capacity in natural soils and ensure acceptable removal rates. The use of high plants and their root-tissue enhanced dissipation on the other hand, has several advantages:

- I. *“Plants improve soil structure and thus aeration and hydrological aspects that may impost limitation biodegradation”*
- II. *“Plants may exude oxidative enzymes that contribute to PAH degradation”*
- III. *“Plants physically translocate organic contaminants into their tissue and then may transform or mineralize the contaminant”*
- IV. *“Plant roots provide easily degradable carbon, energy that generally increases microbial activity in soil, which may lead to enhanced degradation of organic pollutants through direct metabolism or co-metabolism”*

(Yu et al. 2011) – page 1

Those effects can be observed in the rhizosphere, which is the soil volume enclosing a root where parameters, such as physical, chemical and/or biological ones, are altered in vicinity and by the root. The rhizosphere is mostly defined as the region where a depletion of immobile nutrients, necessary for plant growth, such as ammonia (NH_4^+) or phosphate ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$) and an elevated microbial activity is detectable. Latter effect is based on root exudations such as easily available carbon. Also, other parameters such as pH, redox potential, partial pressures of gases e.g. oxygen and moisture might be altered as well. Rhizosphere technology has been observed to have positive effects on the degradation of a wide range of organic pollutants, including PAHs and may be further enhanced by additional input of easily degradable carbon that induces diauxic growth or co-metabolic processes. (Joner and Leyval 2003)

Arbuscular mycorrhiza fungi (AMF) live in symbiosis with most herbaceous plant species and are known to enhance biodegradation of organic pollutants, including dissipation processes of PAHs around the mycorrhizal roots. (Yu et al. 2011) AMFs are typically described as functions of proximity from roots, whereas their abundancy decreases with distance. Their external hyphae can reach densities of over 100m in 1g of soil, (Corgié et al. 2006; Miller et al. 1995) which provides quiet the amount of surface for bacteria.

A paper by (Joner and Leyval 2003) investigated the degradation capacities of two different contaminated soils onto which they planted ryegrass and clover. Ryegrass is widely used for PAH remediation because of its fibrous root system, large specific root surface area (Yu et al. 2011; Corgié et al. 2006) and is often mixed with clover because of its nitrogen fixation capacities. (Meng et al. 2011) The study distinguished between bare soil and vegetation (ryegrass and clover) with as well as vegetation without AMF. The authors found that the soils with AMF showed higher degradation numbers than the soils without.

Also, vegetated soils showed higher degradation numbers than bare soils for both soil samples. The authors explained that various factors, such as the rooting density, fertilization, and watering have strong influencing capacities on AMF growth. (Joner and Leyval 2003) Rhizosphere enhanced degradation is mostly based on plant stimulated microbial activity. However, other factors, such as biological (e.g. bacterial plasmid transfer) or physical (e.g. contaminants in the rhizosphere, modification of soil texture) ones can be of importance. (Meharg and Cairney 2000)

Apart from AMF, also ectomycorrhizal fungi (EMF or ECM) are known to effectively enhance PAH degradation. Arbuscular mycorrhizal fungi (AMF) and ectomycorrhizal (EMF) fungi access nutrients differently: AMF collect nutrients discharged by saprotrophic microbes, while EMF mineralize organic matter to obtain nutrients. (Dong et al. 2018)

(Meharg and Cairney 2000) tested 21 ECM species for the capacity to degrade five different PAHs, namely: Phenanthrene, Anthracene, Fluorene, Pyrene and Perylene. The authors found that 20 could at least degrade one PAH effectively and over half could degrade all 5 PAHs tested for. In contrast to microbial degradation, the ECM exposed to all 5 PAHs, which could not effectively degrade all of the PAHs, showed a preference for 4-5 ring structure degradation, rather than low molecular weight PAHs.

However, it is important to know that most studies investigated AMF and ECM enhanced degradation in laboratory environments that did not internalize aging effects. Yet, some papers took samples from contaminated sites and tested these soils for mycorrhizal activity. (Joner et al. 2006) conducted such a study and reported that PAH degradation was solely observed in non-rhizospheric soils with no mycorrhizal fungi present and therefore concluded that the fungi impeded PAH degradation rather than enhanced it. They explained that the most likely explanation was a lack in mineral nutrients that were otherwise added by researchers reporting a positive feedback on PAH degradation, including their own study from 2003. (Joner et al. 2006; Joner and Leyval 2003)

Root exudates are known to further stimulate the degradation process in vicinity to roots, whereas the process is attributed to the modification and promotion of microbial communities and possibly the introduction of PAH degrading enzymes. (Sun et al. 2010) These exudates can enhance microbial populations and activities 5 to 100 times and pose a mixture of water-soluble sugars, amino acids as well as organic acids. (Técher et al. 2011) The process and the concomitant biodegradation does vary qualitatively as well as quantitatively in between plant species and as a function of plant age, mycorrhizal status and nutrient status. (Joner and Leyval 2003)

Biodegradation based on arbuscular mycorrhiza fungi, ectomycorrhizal fungi and root exudates are together often referred to as *“Rhizoremediation”*, (Denys et al. 2006) wherein prairie grasses, such as the afore mentioned ryegrass, are regarded as *“superior vehicles”* because of their extensive, fibrous root systems and an inherent genetic diversity which gives them an advantage to become established in unfavorable conditions. (Técher et al. 2011) Phytoremediation may as well be combined with other remediation techniques, such as aerobic bioremediation treatment, whereas the remediation processes are carried out in succession. (Denys et al. 2006)

Even though some edible plants are known to transfer PAHs from roots to their edible parts, (Rojo Camargo et al. 2011; Paraíba et al. 2011) the extent of PAH uptake by roots is still discussed: *“Because of their high lipophilicity and low solubility, PAHs would be adsorbed through the epidermis of roots in contact with soil particles, but not drawn along the inner root.”* (p.1) (Meudec et al. 2006) However, some papers investigated PAH uptake via roots on highly contaminated soils. A paper published by

(Fismes et al. 2002) disclosed to have found a direct linkage between PAH concentrations in soil and the content in plants with very low bioconcentration factors. However, no distinction in between root and atmospheric uptake could be made as an alternative explanation suggests PAH uptake via stomata. Another publication has reported to have found evidence for bioaccumulation in internal shoot tissue in *Salicornia fragilis*, wherein the choice of plant with poorly developed leaves minimized possible atmospheric uptake. (Meudec et al. 2006) However, reports on effective PAH bioaccumulation in plants are scarce. This is why, despite the latter publication, phytoremediation is exclusively discussed regarding “*Rhizoremediation*” with no attention drawn to the accumulating process and the concomitant potential removal capacities.

So far, the chapter discussed degradation processes of PAHs in soils. As presented, this is a complex endeavor as degradation processes depend on a wide variety of factors and laboratory results show very different degradation rates as compared to in situ outcomes.

This next part will discuss their fate in the vapor as well as particulate phase. Long range transport processes are mainly accounted for by particle-bound migration, (Lohmann and Lammel 2004) as mentioned previously. However, this is if the compounds have not been scavenged first, since chemical reactions with airborne radicals constitute another main sink for PAHs in the atmosphere. (Keyte et al. 2013)

PAHs in the atmosphere are subject to numerous reactions. The most prominent ones are adsorption processes onto particle surfaces, reactions with oxidant gases like NO_2 , the NO_3 radical, OH radical, O_3 , and SO_3 , and photo oxidation of PAHs due to solar radiation, which is called photolysis. (EFSA 2008) The latter reaction can also occur in surface waters, where PAH half-lives can range from minutes to hours, and on the surface of soils with much longer half-lives. (Niu et al. 2007)

Reactions in the gas-phase with hydroxyl radicals ($\text{OH}\cdot$) are considered to be the prevalent loss process for the more volatile, low molecular weight PAHs, whereas the less volatile, heavier PAHs are mostly lost through heterogenous ozonation and nitration reactions on condensed phases. (Kwamena et al. 2007)

According to (Keyte et al. 2013) the established mechanism of $\text{OH}\cdot$ involves the formation of a PAH hydroxyl adducts and a subsequent reaction with nitrite or ozone, whereas the resulting products comprise both: Ring structures such as nitro-PAHs (NPAHs) or quinones and ring-cleaved compounds like phthalic acid, phthaldehyde and phthalic anhydride. Nitro-PAH formation reactions predominantly start with a nitrate radical ($\text{NO}_3\cdot$) addition, followed by a reaction with nitrite. A major atmospheric sink for vapor PAHs is a decomposition reaction involving $\text{OH}\cdot$. According to (Keyte et al. 2013) the rate coefficients are up to five orders of magnitude higher as compared to the reaction involving $\text{NO}_3\cdot$, for most high molecular weight PAHs with three to four ring structures. Yet, yield numbers suggest that the reaction with $\text{NO}_3\cdot$ poses a considerably higher contribution during nighttime than the reaction with $\text{OH}\cdot$. This is because of the rapid photolysis of $\text{NO}_3\cdot$ (~5sec at solar noon) and the rapid reactions of NO with O_3 and of the NO_3 radical with NO. This is why the $\text{NO}_3\cdot$ concentration generally increases in presence of NO_2 and O_3 after sunset. (Atkinson and Arey 1994) Reactions with ozone on the other hand, are of negligible importance in the atmosphere. (Keyte et al. 2013)

Regarding 2 – 4 ring PAHs, no evidence was found for gas phase photolysis (Atkinson and Arey 1994) and considerable adsorption onto particulates is observed solely in ring structures of 4 or more. (Niu et al. 2007; Harrison et al. 1996) This makes photolysis a degradation process only relevant for PAH degradation intermediates and heavy PAHs.

	OH	NO ₃	O ₃	Photolysis
Naphthalene	6,8 hours	1,5 years	>80 days	-
Acenaphthylene	1,3 hours	6 minutes	~43 minutes	-
Acenaphthene	1,5 hours	1,2 hours	>30 days	-
Fluorene	9,1 hours	1,3 days	>80 days	-
Phenanthrene	11,2 hours	4,6 hours	41 days	-
Anthracene	8,6 hours	-	-	-
Fluoranthene	~2,9 hours	~1 year	-	1,7 hours
Pyrene	~2,9 hours	~120 years	-	2,2 hours

Table 10: Mathematically determined atmospheric lifetimes of various US-EPA PAHs when photolyzed or reacting with gas-phase radicals such as hydroxyl (OH·), nitrate (NO₃·) or ozone (O₃).

Table 10 lists calculated atmospheric lifetimes of 2, 3 and 4 ring vapor phase PAHs if in contact with hydroxyl, nitrate or ozone radicals or if degraded photochemically. Relevant numbers were extracted from (Arey 1998). The study assumed a 12-hour daytime and a concentration of $1,9 \cdot 10^6 \text{ cm}^{-3}$ for the hydroxyl radical, a 12-hour nighttime concentration of $5 \cdot 10^8 \text{ cm}^{-3}$ for the NO₃ radical and $2,4 \cdot 10^{11}$ for NO₂.

The adsorption of PAHs onto particulates constitutes a reactive sink for PAHs in general (Kwamena et al. 2007) and is more prominent for heavier PAHs. (Harrison et al. 1996; Tasdemir and Esen 2007) Surface films/coatings are thought to be developed that shield the adsorbed PAHs from oxidative gases and/or solar radiation. (Kwamena et al. 2007) These coatings depend on the properties of the particle (mineral, organic, carbon and water content), (Jariyasopit et al. 2014) and climatic variations like relative humidity and temperature, which results in distinct effective viscosities of the organic aerosol coating and concomitant distinct reactivities of the PAHs adsorbed onto these particles. (Shrivastava et al. 2017)

Artificial particle substrates include silica, graphite, diesel soot, fly ash, wood smoke, sea salt, organic aerosols, silica, azelaic acid and kerosene soot have been studied vastly in laboratories, mostly artificially coated with a single or a mixture of PAHs, with the goal to derive heterogenous rate coefficients for these reactions. (Jariyasopit et al. 2014; Ringuet et al. 2012)

Table 11 displays partial results of study conducted by (Behymer and Hites 1985) and displays the half-lives for photolysis of various particulate PAHs in hours that were absorbed onto different particles. The evaluated results underline the strong influencing capacities of particle properties in terms of their content, with the highest immobilization capacities by black carbon.

	Silica Gel	Alumina	Fly ash	Carbon Black
Acenaphthylene	0,7	2,2	44	170
Acenaphthene	2,0	2,2	44	-
Fluorene	110	62	37	>1000
Phenanthrene	150	45	49	>1000
Anthracene	2,9	0,5	48	310
Fluoranthene	74	23	44	>1000
Pyrene	21	31	46	>1000
Benzo(a)anthracene	4,0	2,0	38	650
Chrysene	100	78	38	690
Benzo(a)pyrene	4,7	1,4	31	570
Benzo(g,h,i)perylene	7	22	29	>1000

Table 11: Half-Lives (in Hours) for the Photolysis of PAH on Different Substrates

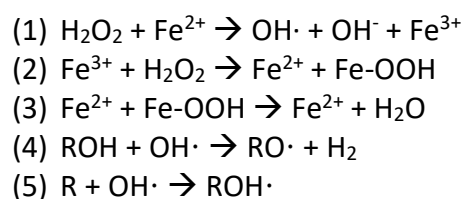
Most studies investigating particulate PAH concentrations in the atmosphere reported major gaps in between mathematically modelled and measured results, wherein the measured results were much higher than the modelled ones. A study by Shrivastava et al. 2017, that reviewed the fate of B(a)P, reported to have found answers that fill this gap. According to their results, the answer lies within particle coating physics. These, so they argue, depend on relative humidity as well as temperature and have the capacity to significantly slow or even shut off the B(a)P oxidation process completely in cool and/or dry conditions. Their insight, so they explained, was based on their understanding of these coatings, whereas they compared their model results to measured results and found that their results highly matched the sampled ones. Additionally, the authors assume, that the heterogenous oxidation products, remain adsorbed on particles instead of being lost and can thus be transported in the atmosphere or may be deposited. (Shrivastava et al. 2017)

The oxidative degradation process can also be used for chemical remediation technology in soils, wherein ozone, hydrogen peroxide - (modified) Fenton's reagent, activated sodium persulfate, potassium or sodium permanganate as well as combinations of these compounds can be used to treat contaminated soils and sediments. (Ferrarese et al. 2008)

Ozone treatments are useful tools because they transform PAHs to an oxygenated intermediate which is more soluble and concomitantly better biodegradable. Remediation techniques are often coupled with injection technology using gaseous and/or dissolved/aqueous ozone. This methods success can be improved by following an integrated strategy, such as extracting the contaminated material first, therefore making it more accessible for ozone and then continue with bioremediation strategies. Reports suggest that high molecular weight PAHs are more susceptible to ozone oxidation. Complementary, biodegradation is more effective for low molecular weight PAHs. (Wick et al. 2011)

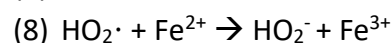
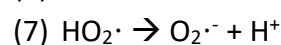
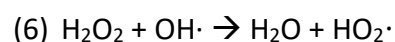
Hydrogen peroxide alone is considered to be insufficiently fast – in terms of kinetics, to degrade most of organic contaminants before its own decay. This is why it is used more often as (modified) Fenton's reagent, which is a mixture of hydrogen peroxide and transition metals that raise radical formation and therefore enhance oxidative strength. (Ferrarese et al. 2008) Peroxide is typically used at concentrations of 3 to 35%, with an optimum pH of 3 – 5 which is necessary to keep the iron soluble in soil solution. If the soil does contain high amounts of iron minerals, such as goethite, hematite or magnetite, additional iron input might be redundant. The chemical reaction itself is exothermic, therefore might enhance volatilization of various compounds and can be managed to some extent with the concentration of peroxide. The removal efficiency of Fenton's reagent is very much depending on the solid matrix characteristics and the contaminant availability (aging, humic substance abundance). (Wick et al. 2011) Contrary to the decrease in PAH bioavailability by humic substances, (Perminova et al. 1999) the organic matter content does enhance peroxide enhanced degradation of PAHs, because those compounds are chemically available and would otherwise be adsorbed into micropores which would render them less chemically available. Yet, larger amounts of organic matter demands higher reagent concentrations because of a hydroxyl radical loss due to scavenging. (Wick et al. 2011)

The reactions 1 – 5 display the process of hydroxyl radical formation and its reactions with organic compounds. Once the hydroxyl radicals have formed, the degradation is either mediated through hydrogen abstraction (4) or hydroxyl addition (5). (Ferrarese et al. 2008)



The effectivity of Fenton's reagents can be enhanced by addition of cosolvents such as ethanol, vegetable oil, surfactants and cyclodextrins that improve extraction of recalcitrant high molecular weight PAHs, which results in increased availability and henceforth degradation. Reactions of PAHs with peroxide results in a high number of oxidation products, mostly quinones, that are generally less toxic and more susceptible to microbial degradation and can also be combined with other remediation approaches. However, combinations with microbial degradation are unpractical because of the low pH necessary to effectively remove PAHs with Fenton's reagent. (Wick et al. 2011; Ferrarese et al. 2008)

Modified Fenton's reagent additionally contains chelating agents and/or high peroxide concentrations. Higher oxidant concentrations induce many complex reactions and numerous reacting species are generated in addition to the hydroxyl radical, such as hydroperoxide ($\text{HO}_2^\cdot$), superoxide anions ($\text{O}_2^{\cdot-}$) and hydroperoxide anions (HO_2^-). These oxidants are very reactive and are known to be able to degrade remarkably recalcitrant compounds. However, very high peroxide concentrations may induce oxidant self-consumption and therefore lead to poor remediation efficiency. The reactions 6 – 8 display the chain reaction that induces their formation with hydrogen peroxide as educt and hydrogen peroxide as reactant, based on its formation reaction (1 – 6). (Ferrarese et al. 2008)

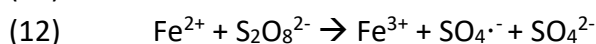
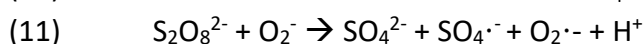
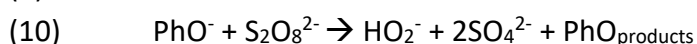
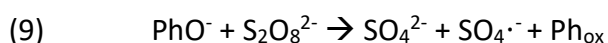


Permanganate (MnO_4^-) is another widely used chemical oxidizing agent for PAH remediation because of its strong oxidizing properties, its capacity to work effectively over a wide pH range and its ability to attack carbon-carbon double bonds of PAH structures. (Ferrarese et al. 2008) Their application may include slow-release devices such as (permanganate)candles for aquatic ecosystems (Rauscher et al. 2012) or ex – situ remediation actions. In aquatic systems, the permanganate salt undergoes a decomposition reaction with cations, such as protons: $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_{2(s)} + 2\text{H}_2\text{O}$. Permanganate reactions are complex and diverse because of its multiple valence states and the reactions are not fully understood yet. (Ferrarese et al. 2008)

Peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$, PDS) and Peroxymonosulfate (HSO_5^- , PMS) are the most recent forms of oxidizing agent being used for remediation purposes. PDS is much cheaper than PMS and longer half-lives in aquifers of 2 to 600 days were reported compared to the half-lives ranging from hours to days of PMS. PDS is most frequently used as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, but also $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$ are common. However, the comparatively high solubility and low cost of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ combined with the increased nitrogen content in soils after application, aiding the recovery of microbial communities, makes it the preferential compound for remediation purposes. Yet, some reports suggest that ammonium (NH_4^+) could also reacts with the sulfate radical and therefore may reduce contaminant degradation. (Zhou et al. 2019)

The adsorption of PAHs onto soil organic matter (SOM) renders the target compound unavailable at first. However, SOM can also increase PAH removal by increasing the formation of reducing agents if persulfate is applied at high pHs. The reaction of how SOM loses its electrons has not been elaborated by the authors. (Ahmad et al.

2010) Reaction 9 displays the initial sulfate radical formation. Reaction 10 is known as the Elbs persulfate oxidation and



activates persulfate using a nucleophilic attack, while the hydro peroxide produced in reaction 10, generates a sulfate radical in reaction 11. Both phenoxide and hydroperoxide can act as persulfate activators at basic pHs. (Ahmad et al. 2010) Persulfate can also be effectively activated by transition metals, such as silver, copper, iron, zinc, cobalt and manganese (see reaction 12). Iron has been widely used because of its low cost and environmental friendliness. (Zhou et al. 2019)

Figure 7 were extracted from a comparative study by (Liao et al. 2019). The study investigated the change of different soil parameters such as TOC and pH, the consequences for the microbial community and removal efficiency of the four discussed oxidative remediation techniques. They analyzed two contaminated soils: "G" A gas plant and "C" a coal plant, extracted soil samples and added the oxidizers under laboratory conditions. CK is a blank and was treated with sterile water, Fenton, M-Fenton and KMnO_4 are self-explanatory while A-PS stands for activated persulfate. All oxidizing agents, except KMnO_4 were activated with iron sulfate.

Figure 7 shows the results after 4 days, as it took that long for the parameters to stabilize. The treatments partly showed large effects on the total organic carbon (TOC) content (figure 7A). Fenton's reagent had no significant effects on the TOC content, but modified Fenton's reagent contained large amounts of citric acid which lead to an increase in soil TOC, whereas the small amounts in A-PS showed no effects on mobilization. The potassium permanganate and activated persulfate samples showed a significant decrease in TOC.

The authors explained that oxidizers in general are unspecific and therefore also consume TOC and that the strong decrease of the samples treated with KMnO_4 and A-PS was related to the high oxidation performances of these oxidizers. Whereas in Fenton's reagent the consumption is related to the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio and leads to a slow TOC decrease. The oxidizers also had significant effects on pH values

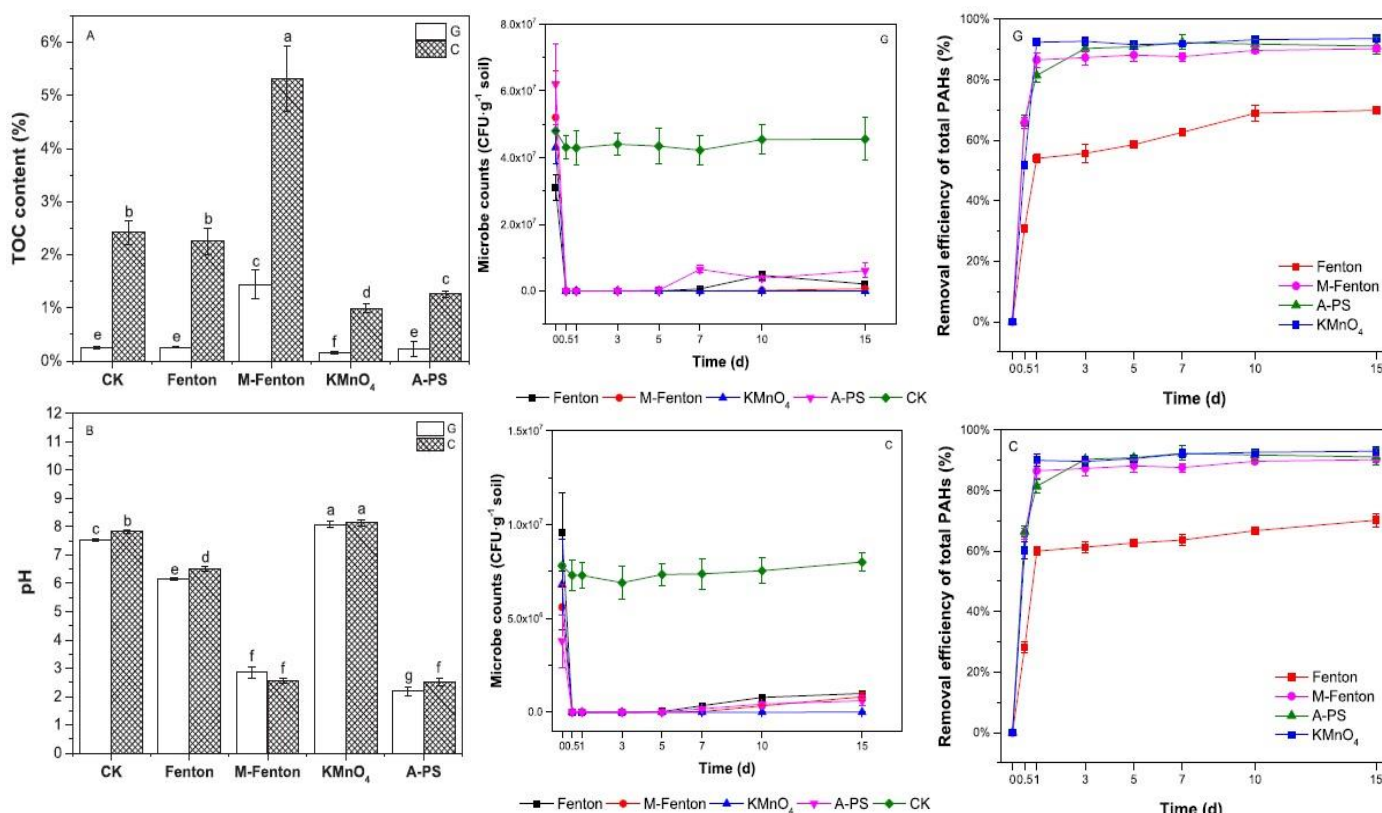


Figure 7: Impacts of various chemical oxidant treatments on TOC (A) and pH (B) after 3 days

Figure 7a: Changes of microbe counts in samples "G" gas plant and "C" coal plant

Figure 7b: Removal efficiencies of total PAHs in samples "G" gas plant and "C" coal plant

in all samples. Yet, the highest impacts were observed in the samples of modified Fenton's reagent and activated persulfate (figure 7B), due to the presence of citric acid and minor but still significant impacts in potassium permanganate and activated persulfate samples were observed.

Since all oxidizing agents act non-specific, they had major effects on soil microbial communities, showing a removal efficiency of 100% at first. However, depending on the reagents, different microorganisms began to grow again, starting at day 7 after oxidant application (figure 7a). Removal efficiencies of about 90%, except for Fenton's reagent, were observed. However, their application has strong impacts on soil physics and the chemical properties of these soils and therefore govern the composition and regrowth of microbial communities and possible follow up bioremediation strategies. Everything from inoculation of strong PAH degrading communities and/or plant species is thinkable. (Liao et al. 2019)

4. Methods

a. Sampling

All sampling sites have been verified to exclude brownfield as well as former landfill sites and not to be located on recent or former industrial or commercial grounds. Sampling locations were mainly attributed by so-called near-natural land use soils (forestry, grassland, agriculture) while a smaller amount was located in settlement areas or in well-established parks and public green spaces maintained unchanged for at least 20 years. Sampling spots were located at least 20 meters from roads or tracks to avoid result distortions.

2167 samples were taken by Saxon LfULG officials from topsoils in between April 2010 and January 2018, whereas topsoils were understood as the top layer with high humus contents as well as root densities according to the German classification system. (Ad-hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe and Bundesanstalt für Geowissenschaften und Rohstoffe 2005)

The sampled soil horizons were classified as A_h (humus topsoil with a mass content below 30%), A_p (plough loosened humus topsoil), A_e (topsoil that classifies as zone of eluviation), as both A_h - A_p or S_w - A_p (S_w means backwater conducting soil parcel and A_p properties - as explained).

	Minimum [cm]	Maximum [cm]	Mean [cm]
Agriculture	5	43	27
Grassland	6	46	24
Forest	2	32	8
Settlement Area	6	38	19

Table 12: Sampling depths according to land use

Table 12 displays the minimum and maximum as well as the mean sampling depths of different land use patterns. Means refer to the deepest point excavated (in cm) during sampling.

The deepest humus rich layers (means) are found in agricultural soils due to tillage practices and concomitant mixing, followed by grassland due to short turnover times compared to forests and

followed by settlement areas because of land use practices that remove dead biomass before combustion and therefore counteract biomass buildup and finally forests.

At the sampling sites, a square shaped area of approximately 1,5m² was excavated and a soil profile was taken. Then, samples were collected from all four walls of the hole from the top organic layer (A-horizon). The extracted soil sample was mixed and approximately 1kg of soil was taken to the lab and analyzed based on German standard procedures [DIN ISO 18287 (09/2008)] regarding PAHs.

At the sampling site, various parameters of the location were recorded and combined with other parameters such as coordinates, mean annual precipitation and temperature into an excel file. That file was used for evaluation during this thesis and included:

The coordinates of the sampling site, the purpose of the sample (which was not primarily PAH analysis), the project during which sampling took place, soil type, soil substrate type, sampling depth, the nature of soil extraction, sampling date, organic matter content, elevation, mean annual temperature, mean annual precipitation, demographic category (rural, fairly populated...), land use category (agriculture, grassland, forest, settlement soil) geological features and the concentrations of the 16 US-EPA PAHs as well as the concentration of the sum PAHs.

b. Categorizations

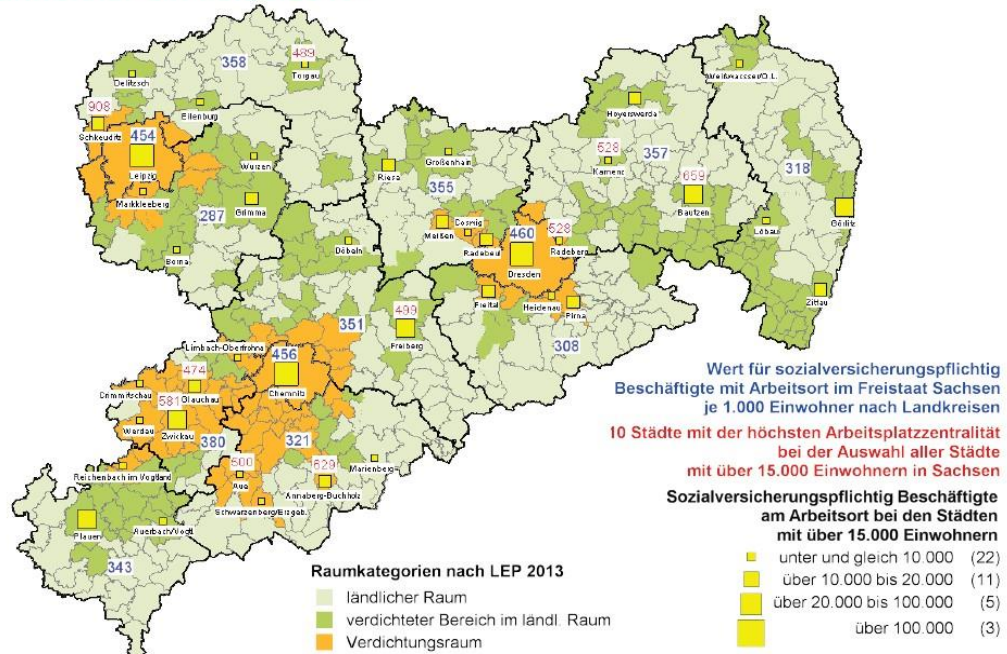
The results were then categorized according to land use patterns and population density of the sampling site since these were judged as key factors influencing PAH concentration in general. This is to gain representative background values for different PAHs and obtain information about possible differences in between concentrations of the individual groups. As sources are mostly of anthropogenic origin, elevated concentrations are expected in proximity to anthropogenic activity. *“Cities are the densest area of anthropogenic activities, owing to the rampant development of industrialization, urbanization, and agricultural modernization, urban soil, as an important part of urban ecosystems, has been suffering most from contamination with various pollutants, such as [...] including PAHs.”*(p.1) (Wang et al. 2018)

Land use categories included agricultural, grassland and forest soils as well as vegetated soils in settlements such as villages, small towns or cities. Latter category includes all kinds of vegetated soils such as parks, gardens, green spaces or other recreational green zones. They were not further specified within the input file at hand and are named “settlement soils” for the purpose of this thesis. Demographic characteristics were grouped as rural areas, fairly populated areas, highly populated areas as well as city areas and determined using the amount of people registered working within the specific catchment zones defined as municipalities of different postal codes.

Figure 8 displays a map of Saxony that differentiates in between the afore mentioned demographical features. The map was created by the state chancellery in 2016 and is based on data of the statistical state office. (Arbeitsplatzzentralität 2016) numbers within the map refer to the amount of people reported per 1 000 inhabitants.

Arbeitsplatzzentralität: Sozialversicherungspflichtig Beschäftigte mit Arbeitsort im Freistaat Sachsen je 1.000 Einwohner am 30.06.2015

SÄCHSISCHE
STAATSKANZLEI



Quelle:

Daten - Statistisches Landesamt des Freistaates Sachsen, Sächsische Staatskanzlei, Referat 32 - eigene Berechnungen

Grafik - Sächsische Staatskanzlei, Ref. 32; Hinweis: Raumkategorien nach LEP 2013; Berechnungsgrundlage - Bevölkerung am 30. Juni 2015

Figure 8: Population density as evaluated by Saxony's state office in 2013. Light green: rural areas; Dark green: Fairly populated areas and Orange: Densely populated

Rural areas are displayed in light green, fairly populated areas in dark green and highly populated areas in orange. Conurbations are visible as yellow squares whereas the size corresponds to the number of inhabitants. The three areas classified and evaluated as cities, namely Dresden, Leipzig and Chemnitz are not additionally marked. However, their locations are discernible as the biggest yellow squares in figure 8. According to the regional development plan published by the statistical state office (Saxony) in 2013, the population categories were separated as following: (Statistisches Landesamt Sachsen 2013)

1. Densely populated areas must fulfill two out of the three following criteria and additionally have an interconnected area with at least 150 000 inhabitants.
 - a. The share of designated settlement and traffic structures must exceed 11,6% of total surface.
 - b. The population density must be higher than 200 inhabitants per square kilometer.
 - c. The settlement density must be higher than 2 000 inhabitants per square kilometer settlement area.

These areas display a high density, not only in inhabitants, living- and work- spaces but also in marked routes, railway lines, plants and institutions that serve technical and social infrastructure as well as a high level of intertwinement in between those characteristics. Aside from big conurbations, densely populated areas may also include rural settlement structures that grew historically into these conurbations and wherein

their characteristics have to be internalized in government as well as development plans.

2. Fairly populated areas are distinguished from rural areas because of their comparatively high population and over proportional share of settlement as well as traffic areas. The boundaries for a category to be determined as “fairly populated” were set at:
 - a. The share of designated settlement and traffic structures must exceed 10% of the total surface.
 - b. They are to be found in vicinity to major conurbations or must show an interconnected area with at least 10 000 inhabitants.
3. Rural areas are defined as areas with less settlement and traffic areas as well as fewer inhabitants compared to the afore discussed “fairly populated areas”. These areas comprise particularly sparse populated areas with a high village density and peripheric location.
4. The classification as “city” was not determined by the regional development plan but introduced as additional, fourth category by the state office for environment, agriculture and geology (LfULG – Landesamt für Umwelt, Landwirtschaft und Geologie). This is because the three administrationally free cities within Saxony’s borders, strongly exceed the minimum requirements for “highly populated areas”, in terms of inhabitants and sealed surface area. The three cities, namely Chemnitz, Dresden and Leipzig have roughly 247 000, 555 000 and 589 000 inhabitants and a share of traffic as well as settlement structures of 44,9%, 42,2% and 54,2%. (Statistik Sachsen 2019a, 2019c) Therefore it is expected that they show a different PAH distribution pattern.

	Rural Area	Fairly populated	Highly populated	Cities	Total
Agricultural Use	437	296	279	10	1022
Grassland	143	114	141	4	402
Forests	220	136	164	4	524
Settlement Areas	62	64	61	32	219
Total	862	610	645	50	2167

Table 13: Sampling details in absolute numbers

Table 13 displays the number of samples taken according to land use and demographic category. Samples from cities are highly underrepresented, constituting only 2,3% of all samples taken. Therefore, evaluation is mostly conducted grouping highly populated areas and cities as one. In some cases, cities are evaluated individually, whereas land use practices are neglected, and a uniform PAH content is assumed within city soils.

Moreover, sampling density varied greatly across the state of Saxony. Even though 73% of the total area of Saxony is allocated to rural areas only 39,8% of samples were taken in these areas. (Univ.-Prof. Dr. Peter Jurczek 2009)

As visible in figure 9, the area west of Chemnitz – towards Zwickau, categorized mostly as highly populated, was sampled greatly in comparison to other locations, such as the rural area towards the southern states border.

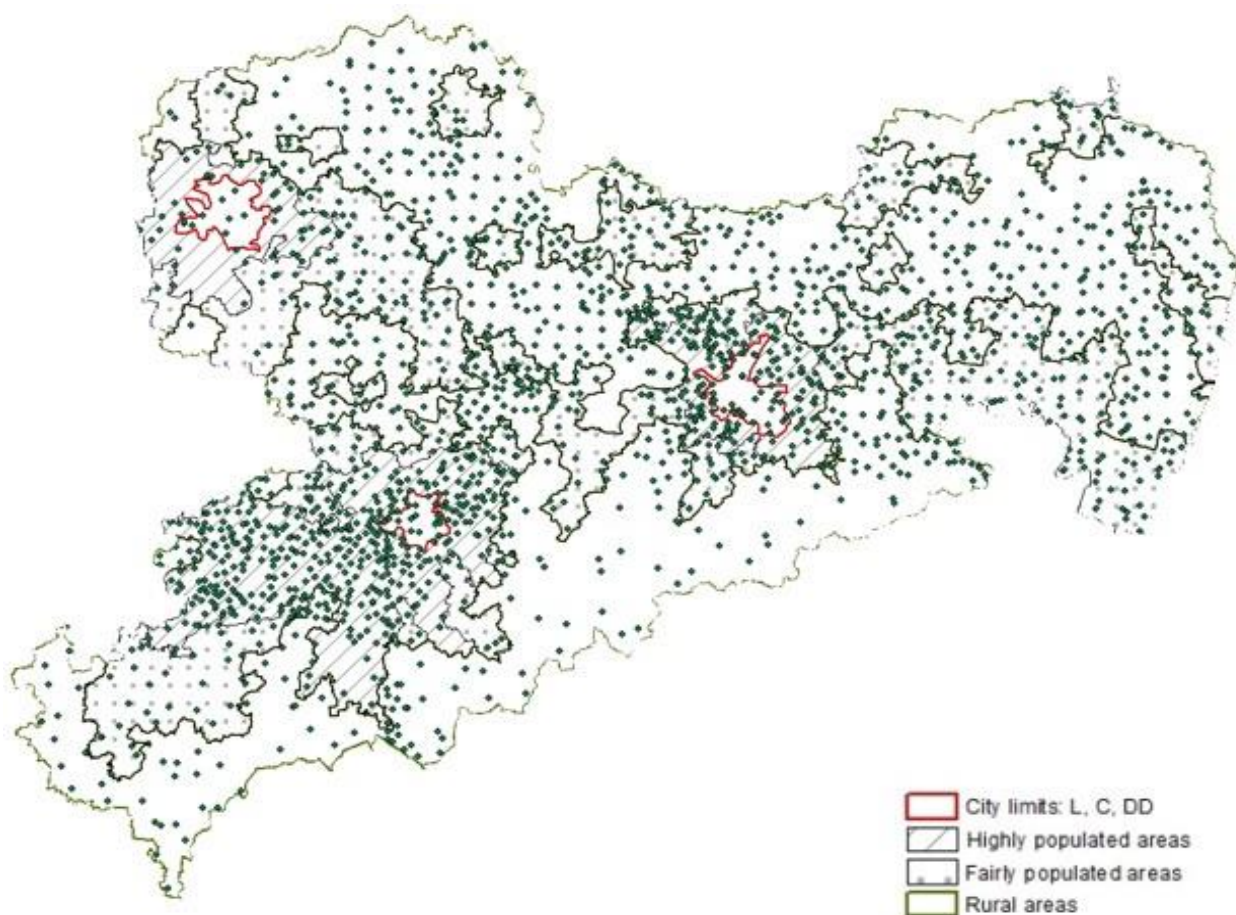


Figure 9: Sampling locations displayed as green dots on the map

c. Background values

The background values of all 16 PAHs and the sum of PAHs were evaluated and expressed as the 50th and 90th percentiles after removing extreme values, wherein outliers and extreme values were determined as:

$$\left. \begin{aligned} \text{Outlier} &= 75^{\text{th}} + (1,5 * (75^{\text{th}} - 25^{\text{th}})) \\ \text{Extreme Value} &= 75^{\text{th}} + (3 * (75^{\text{th}} - 25^{\text{th}})) \end{aligned} \right\} \begin{array}{l} \text{Wherein } 75^{\text{th}} \text{ and } 25^{\text{th}} \\ \text{refer to the} \\ \text{percentiles evaluated} \end{array}$$

In extreme cases, when more than 75% of samples taken, proved to contain PAH contents below detection limit, an alternative approach becomes necessary, as the results of the above listed formulas become zero. To solve this problem, the 75th percentile was set to be 75% of the detection limit and 25th percentile 25% of the detection limit, wherein the detection limit was 2 µg/kg.

And because $0,75 * 2 \mu\text{g/kg} = 1,5 \mu\text{g/kg}$ and $0,25 * 2 \mu\text{g/kg} = 0,5 \mu\text{g/kg}$

The formulas result in:

$$\text{Outlier} = 1,5 + (1,5 * (1,5 - 0,5)) = 1,5 * \text{detection limit} \Rightarrow 3 \mu\text{g/kg}$$

$$\text{Extreme Value} = 1,5 + (3 * (1,5 - 0,5)) = 2,25 * \text{detection limit} \Rightarrow 4,5 \mu\text{g/kg}$$

After recalculating the results without extreme values, the percentiles were evaluated and expressed according to land use and demographic classification.

All values were rounded to two significant decimal places in the interest of not implying misguided accuracy. Additionally, the share of the individual PAHs was determined and expressed by box plots.

d. Low and high molecular weight polycyclic aromatic hydrocarbons

For many objectives it makes sense to distinguish in between low and high molecular weight PAHs as their properties strongly depend on their mass. Some papers distinguish in between PAHs according to their number of rings, others group them into low- medium- and high- molecular weight PAHs, wherein LMW PAHs show 2 or 3 ring structures, MMW PAHs 4 rings and HMW PAHs 5 or more rings. For the purpose of this thesis, LMW PAHs are referred to the more volatile 2 or 3 ring structures and the more stable 4, 5 or 6 ring structures are labelled HMW PAHs.

e. Evaluation of seasonal patterns

In order to evaluate and discuss seasonal patterns of PAHs in Saxony, it is important to first look further into the times of sampling events. This is to say in what months samples were taken as well as the sampling distribution in terms of land use category, as for the sampling was not conducted equally throughout the year nor regarding land use.

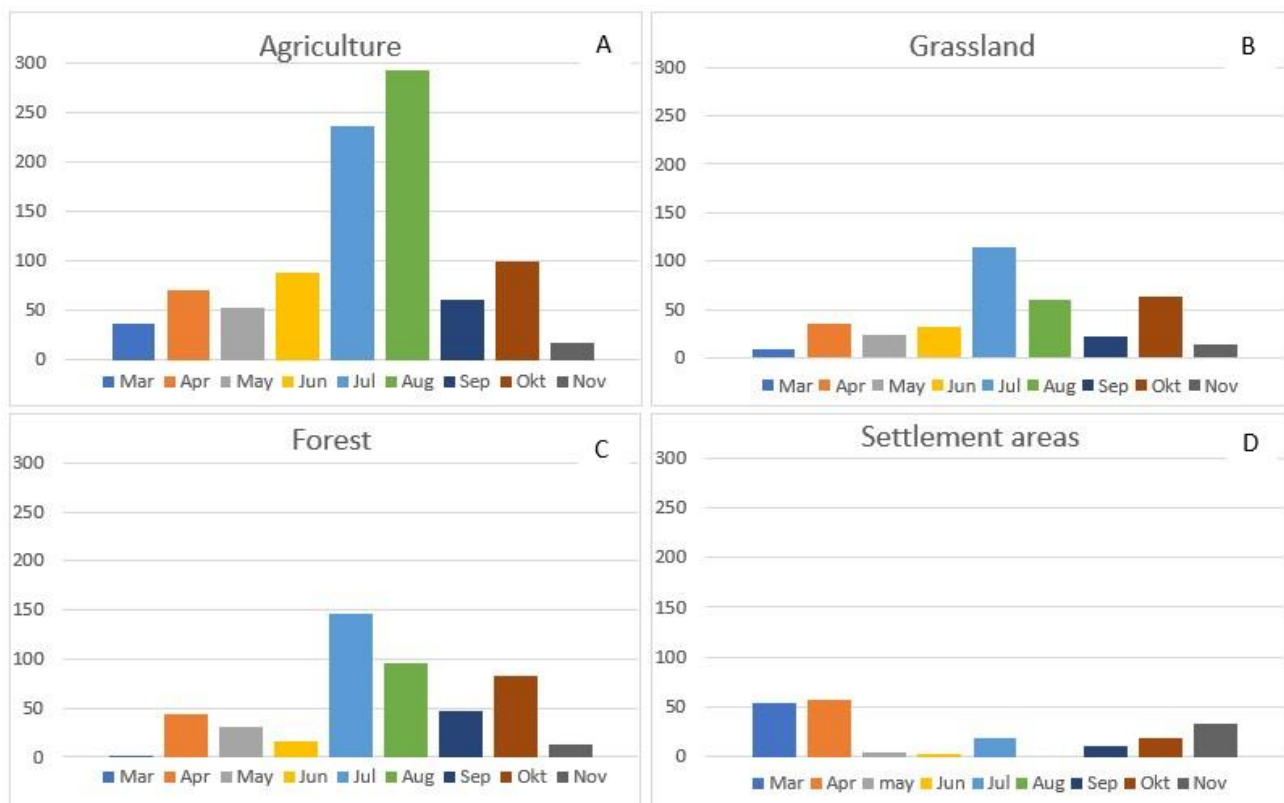


Figure 10: Sampling in absolute numbers per month, over the whole sampling period expressed for the different land use patterns: A Agriculture, B grassland, C forest and D Settlement Areas

Figure 10 displays sampling events per month and distinguishes in between land use categories. Direct correlations in between daily temperatures and PAH content could not be assessed due to the absence of data regarding everyday temperatures and mean annual temperatures proved to be of little use. As for land use categories, figure 10D shows that the sampling events for settlement soils have been based on a single project and are therefore insufficiently distributed for the purpose of a monthly evaluation. However, agricultural, grassland and forest samples were sufficiently sampled to make seasonal pattern evaluation possible and a distinction in between the three conurbations marked as “cities” was possible.

Additionally, because it was expected that seasonal patterns were most likely discernible in cities, daily temperature data was extracted from track records of German weather services belatedly and added to the input file. (CDC - Climate Data Center) Successive testing showed that the distribution was not homogenous (Lavene Test) and further testing regarding intersubject effects showed that the data was unsuited for the purpose of seasonal pattern evaluation. Again, this is due to the sampling practices, wherein most samples were taken consecutively within one and the same catchment area and concentrated in early spring and late fall as well as winter while very little sampling took place during late spring and summer.

The general sampling frequency is displayed in figure 11. Graph A displays sampling events per year while graph B displays them per month and distinguishes in between land use. It becomes clear, that most of the data evaluated originates from the beginning of the last decade with some contribution from the years 2016 and 2017. As for months, most of the samples were taken during the warm summer months July and August.

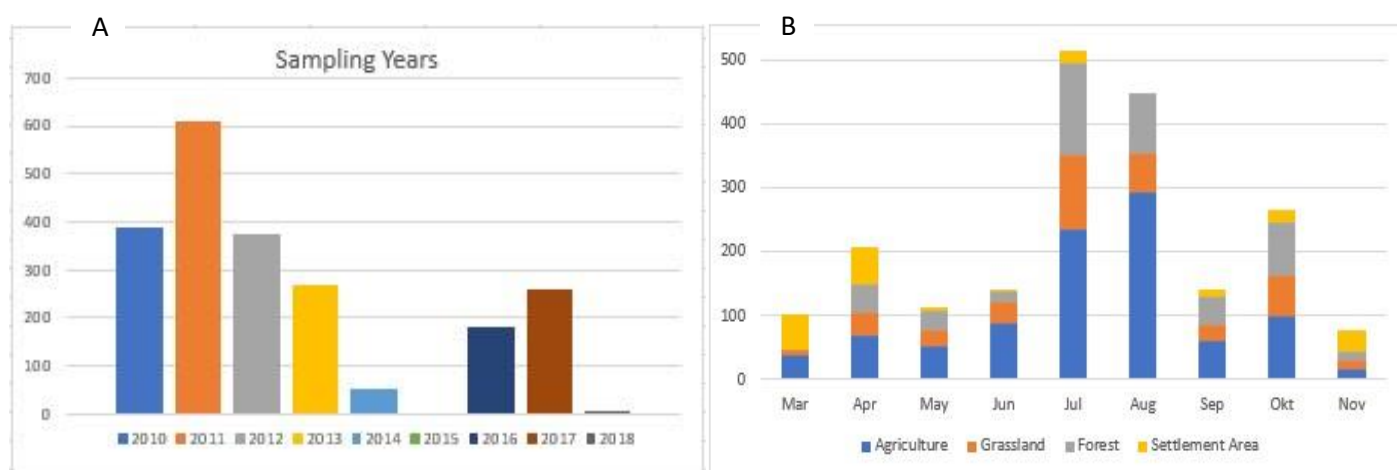


Figure 11: General sampling frequency A per year and B per month

f. Toxicological assessment

As discussed in the chapter “3f toxicity” and toxicological evaluation, there is one problem to be solved in order to assess toxicity within this thesis since not all PAHs were appointed TEFs by German regulation. Therefore, alternative TEF values needed to be added in order to be able to assess all measured PAHs and the five PAHs missing TEFs, were appointed the values determined by. (Nisbet and LaGoy 1992).

The authors are widely cited for their TEFs as they were the first to set them at 0,001. Because the authors set these values quite low, the overall toxicity is not expected to change much at all but were added for the sake of completeness. Table 14 recaptures what was displayed in table 5/6 and shows the TEFs as used for evaluation in the right column.

During evaluation B(a)P threshold exceeds were investigated regarding the threshold values as determined by the decree from 2016 (MLUR 2016), the shares of other PAHs in relation to B(a)P

Compound	Abbreviation	TEFs by German Legislation	TEFs by Nisbet and LaGoy 1992	TEFs used for toxicity evaluation
Benz(a)anthracene	B(a)A	0,1	1	0,1
Benzo(a)pyrene	B(a)P	1	1	1
Dibenz(a,h)anthracene	D(a,h)A	1	0,1	1
Benzo(b)fluoranthene	B(b)F	1	0,1	1
Benzo(k)fluoranthene	B(k)F	0,1	0,1	0,1
Indeno(1,2,3-c,d)pyrene	I(c,d)P	0,1	0,1	0,1
Chrysene	Chry	0,01	0,01	0,01
Anthracene	Anth	0,01	0,01	0,01
Benzo(g,h,i)perylene	B(ghi)P	0,01	0,01	0,01
Fluoranthene	FIA	0,01	0,001	0,01
Acenaphthylene	Acy	0,01	0,001	0,01
Phenanthrene	Phen	-	0,001	0,001
Pyrene	Pyr	-	0,001	0,001
Fluorene	Flu	-	0,001	0,001
Acenaphthene	Ace	-	0,001	0,001
Naphthalene	Naph	-	0,001	0,001

Table 14: TEFs values as set by German legislation, determined by Nisbet and LaGoy 1992 and as used for evaluation within this thesis

followed by a toxicity comparison as suggested by the EFSA. The details for toxicity evaluation were explained in the chapter “3f toxicity” and followed these explanations.

g. Benzo(a)pyrene and sum PAH map

The maps for B(a)P and the sum of PAHs were created using ArcMap. A programme, part of the “package” ArcGIS, that allows to define different layers, whereas these layers can be put on top of one another when generating a map. Within those maps, all data except settlement areas were displayed. This is because the purpose of these maps was to display the general occurrence of PAHs. However, since settlement areas are known to contain higher levels of PAHs than the samples of agriculture, grassland and forests, including them into the maps, would have defeated this purpose. That is, because the concentrations visible within those maps are the result of interpolation processes in between point information (where the samples were taken) given by the input file. In order to integrate settlement area data as well, these results were added later as top layer and are visible as points, discernible by different colors and black edges surrounding them. Barriers were set around these points.

Because of the same argument and the assumption that PAH concentrations are generally higher within city limits, barriers were introduced at city limits, so that these comparatively high values don’t spread into the area surrounding the cities during interpolation procedures. Additionally, values that exceeded the threshold for “extreme values” were cut and set to be at outlier level.

The mapping parameters were set to integrate data from a vicinity of 1000m, up to the nearest 15 data points and the grid size was set at 250 m². Within the program's functions, IDW (Inverse Distance Weighting) was used for interpolation. Wherein, as the name suggests, a weighted average distance value is used to represent the input values. That is why this method is incapable to represent mountain and valley surfaces if those extremes were not initially captured. Best results, using this method are obtained if local reference points are sufficiently close/dense regarding the local variation of values expected, which can be said for virtually all mapping software. (ArcGIS Handbook 2020) But because the sampling density varies across the catchment zone and because one of the least sampled areas – the south border of Saxony (fig. 10) overlaps with Saxony's highest elevations (fig. 1), the accuracy of PAH representation must be discussed.

This thesis was supervised by the LfULG, therefore an elevation layer, provided by LfULG, was on-hand. However, this layer was not used because it may have implied misguided accuracy in areas of high elevation or mountain crest frequency and was unnecessary in areas with high measuring density because of very little geographical elevations regarding the relative points of zero elevation. That is why the mapping process did abstain from the elevation layer.

For the shaping, the programme's "polygon" function was used, wherein the programme created polygons of PAH concentrations according to the most accurate representation. The results were then corrected in terms of small polygons that displayed different concentrations in wide areas of distinct concentrations, as these small polygons were based on single point information and did most likely not represent the local situation accurately.

h. Correlation in between organic carbon and PAH content in soil

The evaluation of humus contents was conducted following the German pedological classification guidelines, wherein seven classes distinguish in between different humus contents. Those classes are displayed in table 15 and are named from h0 to h7, wherein h0 shows no humus content and h7 shows the highest humus content.

These are distinguished by their humus contents with separating values of 1, 2, 4, 8, 15 and 30 mass percent for agricultural, settlement as well as grassland soils and values of 1, 2, 5, 10, 15 and 30 mass percent for forest soils. These values can also be expressed as organic carbon contents, if the humus content is multiplied with a factor of 0,58. (Ad-hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe and Bundesanstalt für Geowissenschaften und Rohstoffe 2005)

Class title	Humus Content	In Agriculture and Grassland		In Forests	
		Mass [%]	C _{org}	Mass [%]	C _{org}
h0	Humus free	0	0	0	0
h1	Very little humus content	<1	<0,58	<1	<0,58
h2	Little humus content	1 – 2	0,58 – 1,16	1 - 2	0,58 – 1,16
h3	Medium humus content	2 – 4	1,16 – 2,33	2 - 5	1,16 – 2,90
h4	High humus content	4 – 8	2,33 – 4,65	5 - 10	2,90 – 5,80
h5	Very high humus content	8 – 15	4,65 – 8,72	10 – 15	5,80 – 8,72
h6	Extreme humus content; Almost boggy	15 - 30	8,72 – 17,44	15 - 30	8,72 – 17,44
h7	Organic material; Peat	>30	>17,44	>30	>17,44

Table 15: Humus classes, content descriptions, mass percent equivalents and organic carbon contents following the German pedological classification guidelines for agricultural and grassland soils as well as forest soils.

However, not all of these classes are represented in the samples taken. Humus contents were found from class h1 to class h6 with different patterns for the distinct land use types. Obviously, the land use types of agriculture, grassland and forest were grouped accordingly, however, settlement area soils were grouped according to the classification regarding agriculture and grassland.

5. Results and Discussion

a. Background values

The tables 16 – 19 show the background values of the 16 US-EPA PAHs. They are displayed as the 50th and 90th percentile, also the number of samples used to evaluate the percentiles, excluding the ones that exceeded the threshold for “extreme values”. The 50th percentile values are used to represent typical pollution levels, whereas the 90th percentile is applied as threshold value to pinpoint high pollution levels.

The results are grouped according to utilization and demographic categories, wherein “*rural*” stands for rural areas, “*fairly*” represents “fairly populated” areas and “*highly*” depict “highly populated” areas. The latter group combines the results from highly populated areas and cities.

DL stands for “*detection limit*”. Therefore <DL indicates that the respective percentile is located below detection limit. Values below detection limit are only found for the 50th percentiles of the individual PAHs while all 90th percentile values surpass the detection limit or could be determined mathematically.

50th percentile values below detection limit were predominantly found in rural areas and/or agricultural soils where pollution levels are comparatively low. Agricultural topsoils are subject to dilution due to tillage practices which contributes to comparatively low values.

Furthermore, all low molecular weight PAHs except for Phenanthrene, showed at least one percentile below detection limit. The high molecular weight PAHs on the other hand, displayed a lone representative with only one value below detection limit, namely the 50th percentile of Dibenzo(a,h)anthracene in rural agricultural soils. The following paragraph will discuss all percentiles below detection limit, tables 16 to 19 may serve as more comprehensive depictions for the discussion. Acenaphthene is the compound that presented most values below detection limit. The values in agricultural, grassland and forest soils for all demographic categories showed a 50th percentile below detection limit. Second on the list is Fluorene which showed an almost identical pattern. Only one more percentile could be determined for Fluorene, namely the 50th percentile for forest soils in highly populated areas. Therefore the 50th percentiles for agricultural and grassland soils for all demographic categories except settlement areas, as well as agricultural and forest soils in highly populated areas were found below detection limit.

Acenaphthylene doesn’t show as many values below detection limit. Still, the 50th percentile for all rural land use categories, except settlement areas, and agricultural as well as grassland soils in fairly populated areas is to be found below detection limit.

Naphthalene shows three values below detection limit. The 50th percentile of agricultural soils in rural and fairly populated areas as well as grassland soils in rural areas are located below detection limit. Finally, Anthracenes 50th percentile in rural agricultural soils is located below detection limit.

Noticeably, the 50th percentiles below detection limit were almost exclusively found for low molecular weight PAHs and none of them in settlement areas. As discussed in the chapter *“3c What are priority PAHs and what makes them a priority substance”*, the 16 US-EPA PAHs refer to the most frequently encountered PAHs. However, their frequency of occurrence was determined by emission factors calculated for specific sources and general abundance in highly polluted environments. (Simon et al. 2007; US EPA 2005)

Yet, the results within this thesis refer to natural soils of little polluted areas in temperate regions, where much of PAH contamination is suspected due to historic deposition from air to soil that relaxed to an equilibrium on a multi-year time scale. (Keyte et al. 2013) Therefore, this determination does not internalize partitioning nor (re)volatilization processes of the more volatile low weight PAHs, that are known to be more mobile than their heavy relatives. (Abdel-Shafy and Mansour 2016) Additionally, low molecular weight PAHs are degraded faster due to increased bioavailability as well as decreased sorption to soil organic matter, rendering the contaminants more accessible for microbes. (Perminova et al. 1999; Paraíba et al. 2011) The fact that most of the percentiles below detection limit were predominantly evaluated in areas with no significant continuous PAH input supports this argument.

Another reason for low LMW PAH concentrations might be the sampling practice. Although put into glass vessels, the samples were not treated as if they contained volatile compounds and therefore were neither frozen nor covered with methanol when extracted and transported to the lab. In the lab, samples have been air dried, sieved and mixed intensively. Even though they were then relocated in tight polyethylene containers, it is very well possible that a significant portion of these compounds evaporated during sample processing.

µg/kg dry weight		Benzo(b)fluoranthene			Fluoranthene			Benzo(a)pyrene			Dibenzo(a,h)anthracene		
		Rural	Fairly	Highly	LR	LR	LR	Rural	Fairly	Highly	Rural	Fairly	Highly
Agricultural soils	Number	417	280	412	412	412	272	417	278	273	423	287	278
	P50	15	17	150	150	150	56	14	16	28	<DL	2,0	5,0
	P90	48	51	500	500	500	170	45	45	79	9,1	10	13
Grassland soils	Number	133	112	131	131	131	138	134	111	136	138	113	138
	P50	15	23	150	150	150	61	14	21	29	2,5	4,0	5,9
	P90	54	65	520	520	520	250	50	60	100	10	12	16
Forest soils	Number	211	130	213	213	213	161	215	129	163	214	134	164
	P50	22	29	200	200	200	59	13	22	25	3,0	5,0	8,0
	P90	92	94	720	720	720	230	47	63	94	13	17	24
Settlement Areas	Number	59	61	58	58	58	88	57	61	88	57	59	87
	P50	100	120	1100	1100	1100	400	82	120	170	15	19	27
	P90	600	640	6700	6700	6700	1700	490	690	750	72	98	99

Table 16: Background values of Benzo(b)fluoranthene, Fluoranthene, Benzo(a)pyrene and Dibenzo(a,h)anthracene, the number of samples - excluding extreme values, expressed as 50th and 90th percentile

µg/kg dry weight		Benzo(k)fluoranthene			Benzo(g,h,i)perylene			Indeno(1,2,3-c,d)pyrene			Naphthalene		
		Rural	Fairly	Highly	LR	LR	LR	Rural	Fairly	Highly	Rural	Fairly	Highly
Agricultural soils	Number	413	281	270	421	284	278	414	277	274	428	286	280
	P50	12	13	18	17	20	26	11	12	22	<DL	<DL	3,0
	P90	34	40	53	43	47	67	36	38	67	4,0	5,0	13
Grassland soils	Number	131	112	137	134	111	137	135	111	136	137	112	138
	P50	10	15	19	16	22	29	13	18	25	<DL	2,0	3,1
	P90	31	48	73	39	48	75	43	53	80	7,0	9,5	17
Forest soils	Number	213	130	164	213	133	164	213	131	163	210	130	158
	P50	14	18	27	19	26	34	18	26	38	4,0	3,4	5,0
	P90	46	58	95	52	67	93	72	82	120	20	20	18
Settlement Areas	Number	58	61	88	58	61	87	58	61	88	57	55	90
	P50	64	78	110	80	89	130	74	97	150	6,4	7,1	14
	P90	330	390	450	400	520	500	470	520	550	30	33	67

Table 17: Background values of Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Indeno(1,2,3-c,d)pyrene and Naphthalene, the number of samples - excluding extreme values, expressed as 50th and 90th percentile

µg/kg dry weight		Acenaphthylene			Acenaphthene			Fluorene			Phenanthrene		
		Rural	Fairly	Highly	LR	LR	LR	Rural	Fairly	Highly	Rural	Fairly	Highly
Agricultural soils	Number	412	285	280	421	283	276	421	280	283	411	275	273
	P50	<DL	<DL	3,0	<DL	<DL	<DL	<DL	<DL	<DL	9,4	12	22
	P90	3,0	3,0	9,0	1,2	1,1	3,0	2,0	1,4	3,0	32	31	81
Grassland soils	Number	134	111	137	130	109	137	134	111	138	130	110	135
	P50	<DL	<DL	3,0	<DL	<DL	<DL	<DL	<DL	1,4	9,4	16	24
	P90	3,0	4,0	8,0	1,6	1,7	5,2	2,3	3,0	4,4	37	52	100
Forest soils	Number	217	132	164	210	126	163	215	129	161	214	126	159
	P50	<DL	2,0	3,0	<DL	<DL	<DL	<DL	<DL	<DL	15	19	27
	P90	5,0	6,0	8,9	1,3	2,1	4,0	3,4	5,0	6,0	59	67	110
Settlement Areas	Number	57	59	89	55	58	86	57	57	87	58	58	88
	P50	6,0	7,1	14	3,0	5,1	8,2	4,0	5,4	8,0	76	100	160
	P90	32	36	50	21	20	42	32	23	41	610	420	790

Table 18: Background values of Acenaphthylene, Acenaphthene, Fluorene and Phenanthrene, the number of samples - excluding extreme values, expressed as 50th and 90th percentile

µg/kg dry weight		Anthracene			Pyrene			Benzo(a)anthracene			Chrysene		
		Rural	Fairly	Highly	Rural	Fairly	Highly	Rural	Fairly	Highly	Rural	Fairly	Highly
Agricultural soils	Number	410	273	268	411	274	273	410	273	272	410	274	273
	P50	<DL	2,0	4,3	21	25	43	8,0	10	22	12	15	26
	P90	7,0	7,0	13	70	69	140	32	32	74	39	41	81
Grassland soils	Number	135	110	131	134	112	138	132	109	135	134	110	134
	P50	2,0	3,0	4,0	20	34	49	10	16	25	15	21	29
	P90	10	11	20	76	100	200	44	48	97	49	50	96
Forest soils	Number	215	128	162	215	128	161	212	123	163	210	130	162
	P50	2,0	3,0	4,8	20	30	46	10	13	24	18	26	40
	P90	7,0	11	17	79	110	170	34	45	95	74	97	150
Settlement Areas	Number	59	57	86	58	54	84	57	59	88	58	59	88
	P50	19	21	31	190	220	320	93	120	180	100	120	180
	P90	160	110	160	1100	1200	1500	440	670	810	490	600	760

Table 19: Background values of Anthracene, Pyrene and Benzo(a)anthracene and Chrysene, the number of samples - excluding extreme values, expressed as 50th and 90th percentile

Figure 12 displays the relative abundance of the 16 PAHs investigated. The graph does not distinguish in between utilization nor demographic patterns. However, when the compounds are evaluated by category, changes are not discernible graphically.

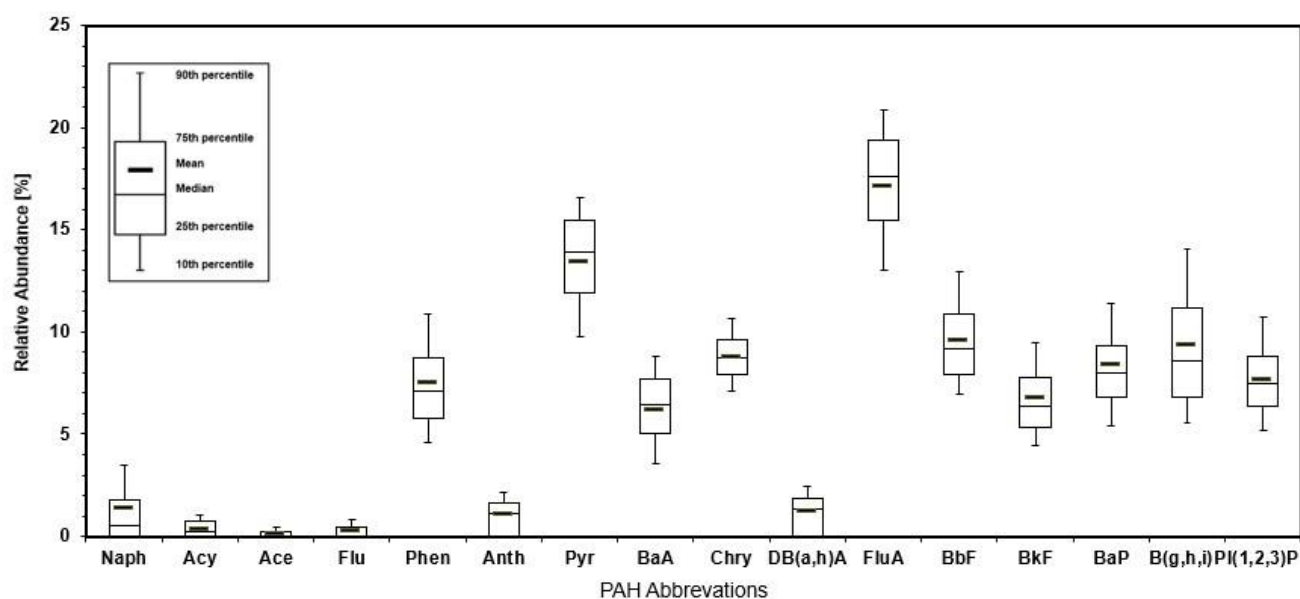


Figure 12: Relative Abundance of the 16 US-EPA PAHs

The 6 compounds [Naph, Acy, Ace, Flu, Anth and DB(a,h)A], that showed 50th percentile values below detection limit, are also the ones that occur relatively little to other PAHs. Table 20 shows the mean relative occurrences of these PAHs when distinguished by utilization and demographic categories. Their occurrence for most cases does not exceed 2 percent, with Naphthalene in forest soils being the only exception.

Even though these values do not show big changes in distinct categories, it is noticeable that the general trend suggests an increase with increasing population density and the concomitant pollutant input that goes along with anthropogenic activity.

Yet, settlement areas need to be treated as an exception because they are located in highly frequented zones in all demographic categories which implies increased PAH input by e.g. household combustion systems including wood-burning fireplaces and car engines, resulting in relatively stable values across the three demographic categories.

Also, the relative numbers increase with the displayed sequence of utilization categories, wherein agricultural soils show the lowest values, followed by grassland, forest and settlement soils.

All values in [%]		Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Anthracene	Dibenzo(a,h)anthracene
Agriculture	Rural	0,74	0,19	0,09	0,15	0,92	0,86
	Fairly	0,85	0,23	0,10	0,17	1,1	1,0
	Highly	1,3	0,69	0,14	0,52	1,3	1,4
Grassland	Rural	1,0	0,29	0,14	0,25	0,99	1,1
	Fairly	1,5	0,41	0,10	0,28	1,3	1,3
	Highly	1,4	0,62	0,20	0,36	1,4	1,4
Forest	Rural	3,2	0,36	0,11	0,34	0,71	1,5
	Fairly	2,1	0,44	0,15	0,46	1,0	1,6
	Highly	2,2	0,47	0,15	0,54	1,0	1,8
Settlements	Rural	0,74	0,53	0,37	0,44	1,8	1,5
	Fairly	1,1	0,53	0,41	0,46	1,7	1,4
	Highly	1,0	0,66	0,40	0,41	1,8	1,3

Table 20: Mean relative occurrence of the 6 PAHs that showed low 50th percentile values

However, Naphthalene seems to be an exception to this general behavior. The compound is often identified to have exceptional behavior because of its properties. Its vapor pressure is two orders of magnitude higher and its solubility double the amount as compared to the PAH closest to the properties of Naphthalene. This makes Naphthalene the uttermost mobile PAH and may explain the pattern observable in table 20. The highest relative shares were observed in forest soils, which is most likely based on the forest filter effect wherein the vertical profile of vegetation traps airborne Naphthalene, probably on the epicuticular waxes of the leaf surface. Another reason is, that the forest canopies shield forest soils from solar radiation resulting in lower temperatures as compared to agricultural, grassland or forest soils, which leads to less Naphthalene evaporation. The chemical is almost exclusively found in its vapor phase at standard conditions (Keyte et al. 2013) which explains the enhanced capturing capacity by forests for this compound compared to the other five PAHs displayed in table 20. Previous studies that investigated PAH profiles in Germany's forests found a high level of Naphthalene as well as Phenanthrene in eastern Germany's O-horizons, including Saxony. (Aichner et al. 2015)

b. The sum PAH

Until now, the relative occurrences of single PAHs, mostly of the more volatile fraction, were discussed.

The big picture governing the occurrence of PAHs is more evident when looking at the sum of all PAHs as LMW PAHs only account for roughly 10 to 14% of all 16 PAHs over all categories.

Table 21 displays the 50th and 90th percentile and the number of samples considered during evaluation.

Again, the observed values rise along with increasing population density from rural to highly populated areas and with the displayed sequence of land use practices from agricultural to settlement soils.

In essence, little change is observed between agricultural, grassland and forest soils.

For example: The percentile values for rural agricultural and grassland soils are almost identical. Even though this is not the case for any other spatial nor utilization category, big changes can only be observed in comparison to settlement areas. The spatial pattern, which will be displayed in greater detail within the section "maps", reflects the distribution of major emission sources, in this case: highly industrialized and/or urbanized areas.

$\mu\text{g/kg dry weight}$		Sum PAH		
		Rural	Fairly	Highly
Agricultural soils	Number	412	277	272
	P50	150	190	310
	P90	500	500	930
Grassland soils	Number	131	111	136
	P50	150	250	330
	P90	520	640	1200
Forest soils	Number	213	130	163
	P50	200	270	390
	P90	720	900	1400
Settlement Areas	Number	58	58	88
	P50	1100	1400	2100
	P90	6700	7200	9500

Table 21: Background values of sum PAH - excluding extreme values, expressed as 50th and 90th percentile

Figure 13 demonstrates graphically how the 50th and 90th percentiles values of the three utilization patterns [A] and [C] act in comparison to the values of settlement areas [B] and [D]. The graphs with and without settlement areas are both displayed because the lower values of agricultural, grassland and forest soils could otherwise not be differentiated with the bare eye as the scaling changes drastically with the inclusion of settlement areas.

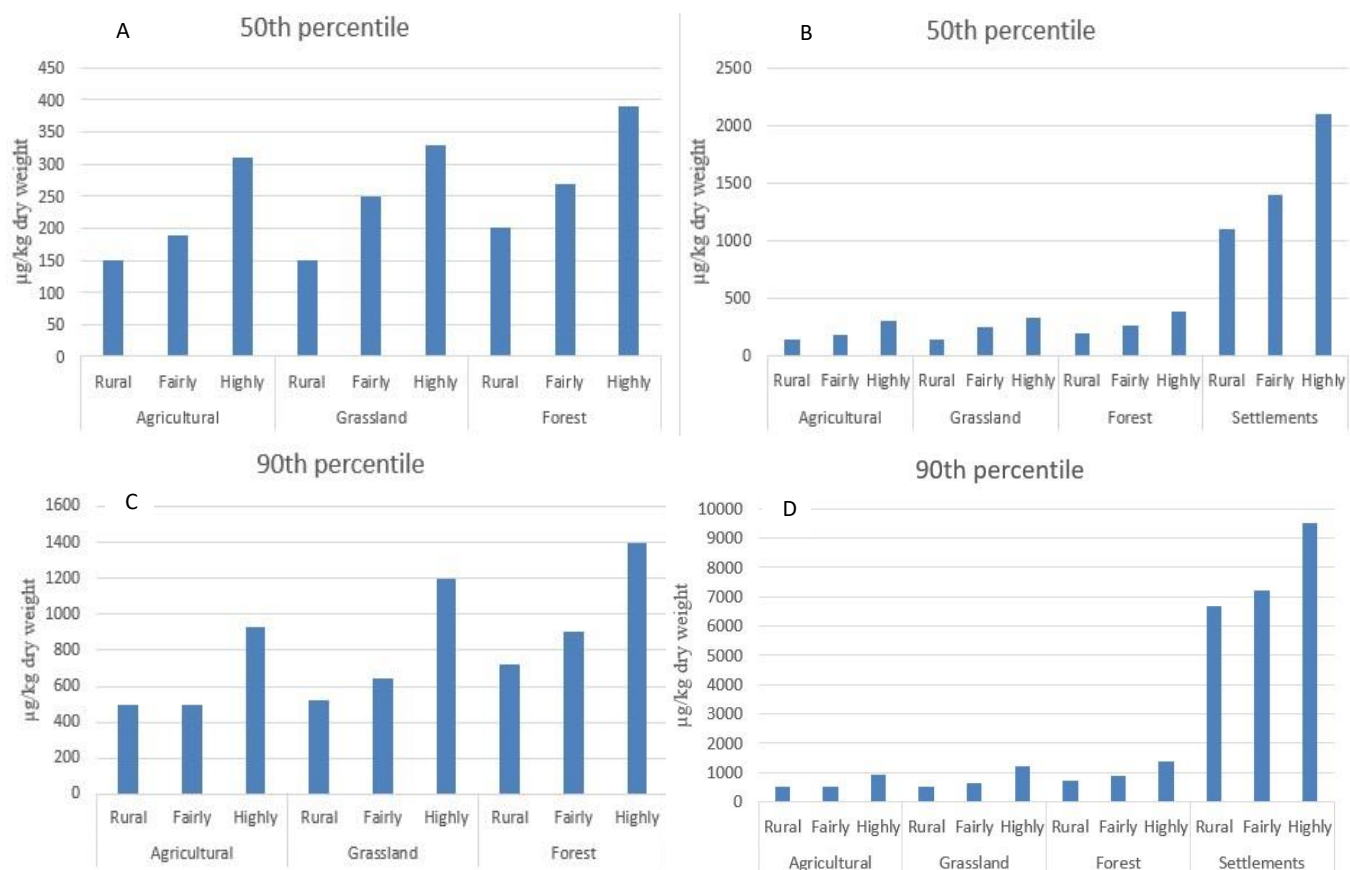


Figure 13: The 50th and 90th percentiles of A: The 50th percentile of Agricultural, Grassland and forest soils of all three spatial categories and; B the 50th percentiles of all four utilization patterns as well as all three spatial categories; C: The 90th percentile of agricultural, grassland and forest soils of all three spatial categories and; B the 90th percentiles of all four utilization patterns as well as all three spatial categories.

Absolute percentile numbers of PAHs in all categories can be seen in table 21. However, figure 13 demonstrates the scale of PAH content beautifully wherein for both percentiles, the 50th percentile values in settlement areas exceed the ones in agricultural, grassland and forest areas 5 to 7-fold and 8 to 14-fold for 90th percentile values.

Again, the argument of constant high deposition explains the high values in settlement areas where anthropogenic activity is highest compared to soils with little activity.

c. Approaching the data & finding patterns

Principal Component Analysis (PCA) was used to take a first look at the data table, wherein in a first step only PAH concentrations were used for analysis. The method revealed two principal components. Component 1 with an Eigenvalue of 14,6 that explains 77% of the data set. Component 2 displayed an Eigenvalue of 2,8 and accounts for 15% of variance. Cumulated both components explain 92% of variance observed.

As Figure 14 shows, all HMW PAHs are represented by component 1 with Acenaphthylene (Acy) as the only LMW representative within this component. Component 2 on the other hand accounts for LMW PAHs including the SUM of LMW PAHS, that incorporates Acenaphthylene (Acy). Conclusively, Acy does not follow the same behavior as other LMW PAHs.

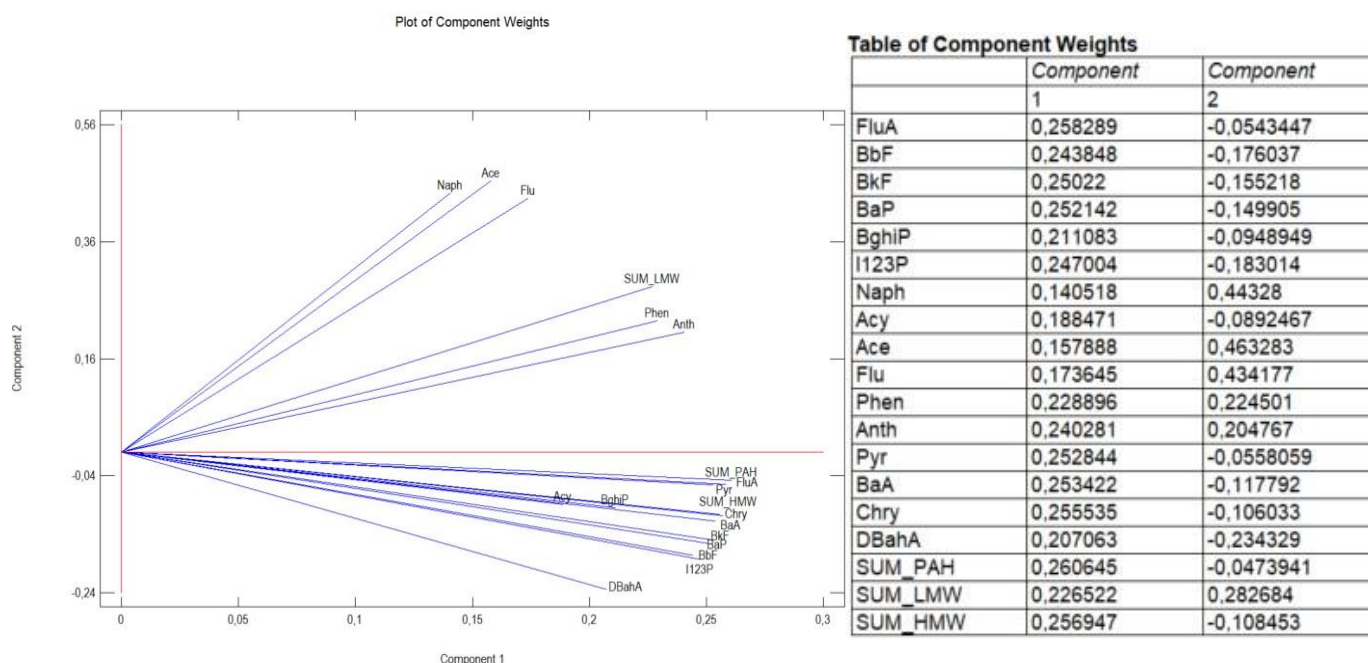


Figure 14: PCA of initial Data set and the corresponding table of component weights

Additional PCAs including other (natural) variables recorded and added in the data set, such as elevation, mean annual precipitation and temperature or the humus content resulted in little changes. Even though an additional component was extracted, the Eigenvalues of the two major components did not change much (14,6 and 3,1) while the percent of variance accounted for decreased to 64% for component 1 and to 13% for component 2 – cumulated 77%. The additional component was represented by elevation, mean annual temperature and precipitation. These three variables correlated strongly to one another ($> \pm 0,88$ Pearson Correlation & $>95\%$ CI) wherein temperature correlated negatively to precipitation and elevation and vice versa but had little explanatory meaning regarding PAHs to Pearson correlations below 0,06 at $CI > 95\%$.

Graphical evaluations (of the PCA, MDS based on Bray Curtis Similarity) of the first PCA components related to land use and demographic categories was inconclusive. As next step the data was transformed using the square root as it is the mildest form of transformation. This was done to find patterns, indiscernible in the original data set as well as cluster behavior. followed by another PCA and a graphical evaluation using different spatial and land use categories with the purpose of finding a pattern.

As figure 15 displays, using the square root lead to increased cluster separation while decreasing the scale. The data was found to be reduced to only one principal component with an Eigenvalue of 16,9 accounting for 87% of the variance. The second principal component showed an Eigenvalue of 0,9 that only explained 4,8% of variance.

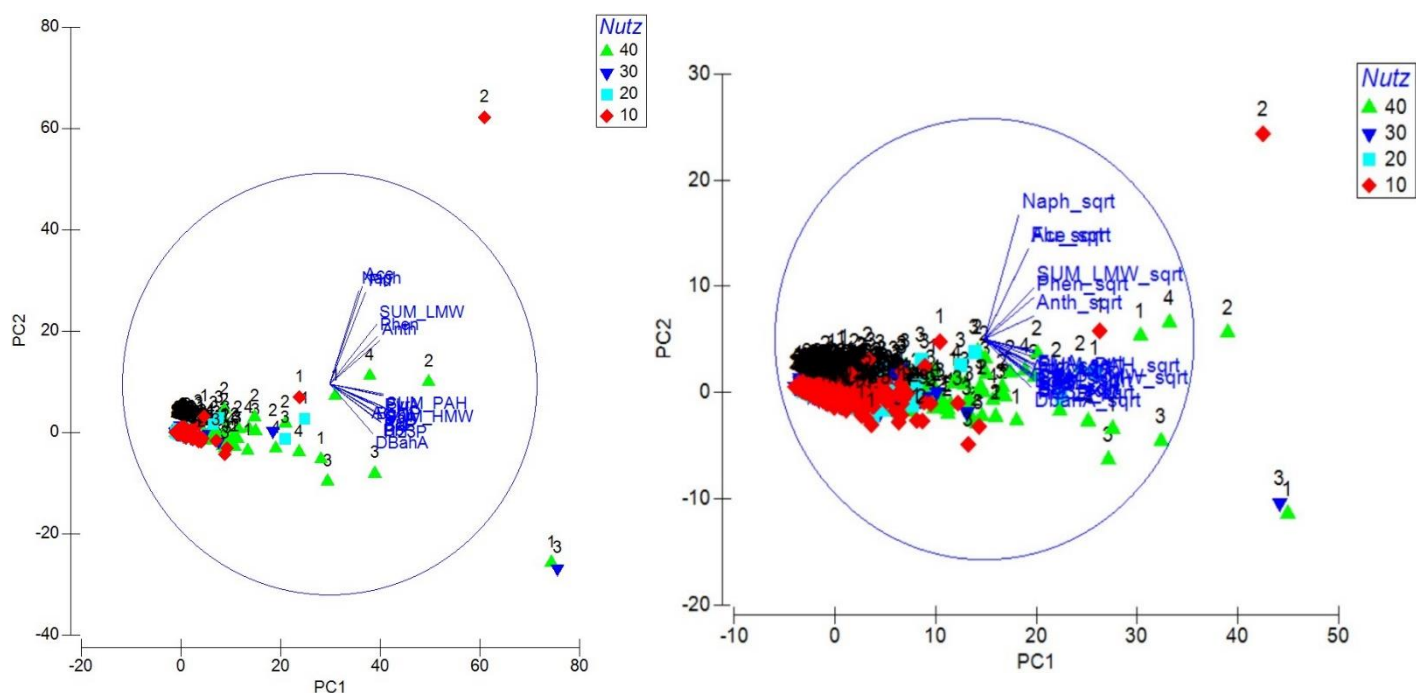


Figure 15: Graphical evaluation of PCA with initial Data set [left] and the data set transformed by square root [right]

Within figure 15, The colored symbols represent different land use categories. 10 (red) represents agricultural, 20 (turquoise) grassland, 30 (blue) forest and 40 (green) settlement soils. The numbers 1 to 4 illustrate the demographic categories. 1 stands for rural areas, 2 for fairly populated areas, 3 for highly populated areas and 4 for city areas.

As component 1 represents HMW PAHs, Acenaphthylene and the Sum PAH that account for 77% of variance, this components pattern equals the distribution explained in the previous chapter's "Sum PAH" of background values. Component 2 on the other hand proved to act differently.

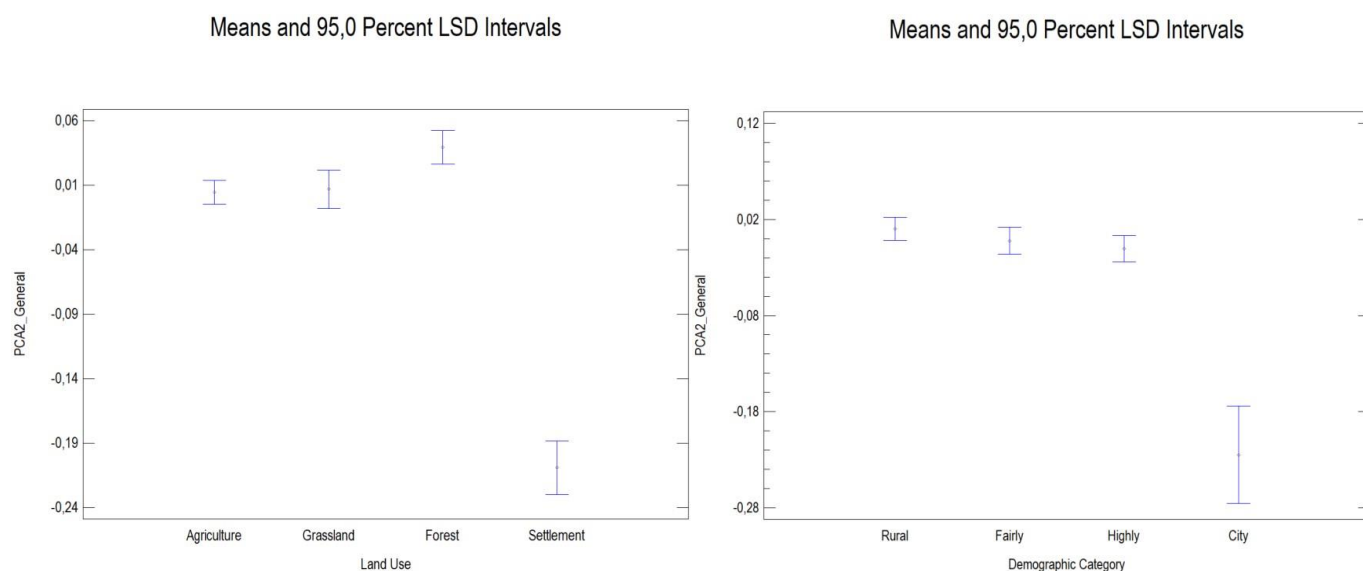


Figure 16: ANOVAs of Component 2 according to land use category [left] and demographic category [right]

Figure 16 displays ANOVA of component 2. These are far lower in settlement and city soils compared to other categories. Regarding land use categories at 95% LSD forest soil values are also significantly higher than values of other categories, whereas a significant difference between agricultural and grassland soil was found at 10% LSD. Differences for demographic categories were of less significance.

A difference between rural areas and highly populated ones was found at a level of significance of 85% LSD, in between rural and fairly populated areas at 60% LSD and in between fairly and highly populated areas at 40% LSD.

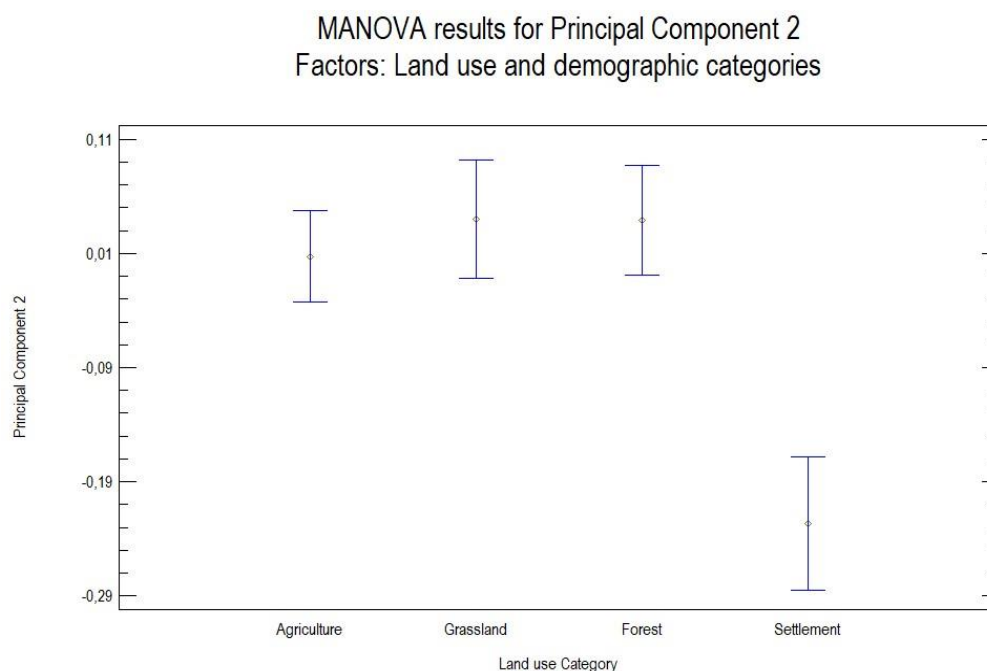


Figure 17: MANOVA means plot including error bars of principal component 2

MANOVA results are visible in figure 17, displaying land use categorizations on the x – axis as they showed that land use has a greater impact on component 2 values (99,9%) than demographic categories (91%).

d. Seasonal patterns

In temperate regions, seasonal patterns are usually discussed in terms of volatile PAH concentration – displayed as changes compared by consecutive months, assuming that a drop in concentrations is expected during warm summer months as compared to colder spring and autumn months.

In Germany summer begins in between the 20th and 22nd of June and ends the 22nd or 23rd of September, whereas a rise in temperatures during June, July and August is to be expected. However, since sampling was not conducted homogenously throughout the year in terms of categorical distribution, an overall evaluation displays a biased seasonal pattern of all PAHs, including HMW PAHs.

Figure 18 displays the means of the sum PAH (16 EPA PAHs) without categorial differentiation and excluding extreme values. At 95% LSD (Least significant difference) and Kruskal Wallis (KW) test results above 95% a significant drop in concentrations measured from March to May is detected. Then concentrations remained at a stable level during May, June, July and August, followed by a slight but negligible increase during September and October followed by a sharp increase in November. Yet, March, April and November were when most settlement soil samples were taken. Even though it was not possible to evaluate seasonal patterns for settlement soils, due to insufficient data density and reproducibility, the sheer number of samples taken during colder months increases the overall means during those months.

A similar pattern was observed for LMW PAHs but was disregarded for the same reasons. Instead, seasonal variation was evaluated for the categories of agricultural, grassland and forest soils by

Means of Sum PAH at 95% LSD

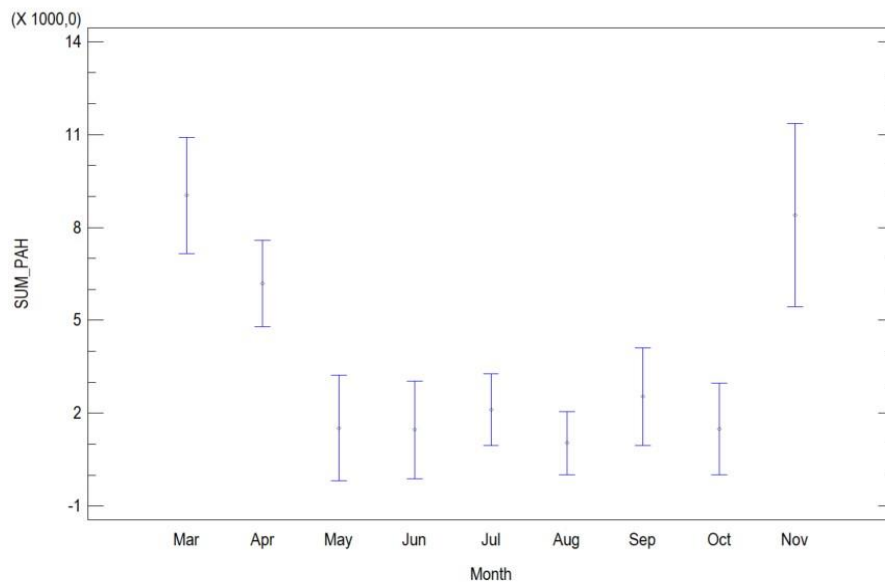


Figure 18: Means of SUM PAH (16 EPA PAHs) at 95% LSD by month from March

investigating means of concentration as well as means of relative abundance [%] as latter evaluation proved to display the above-mentioned pattern clearer. Samples taken in November were excluded as sampling frequency proved to be insufficient to provide acceptable variance homogeneity, concomitantly results proved to be of little significance (visible as error bar extents in figure 18).

Furthermore, samples from highly populated areas were excluded as they displayed a much higher share of LMW PAHs. The same behavior of LMW PAH shares was observed for all utilization categories except forest soils. Forest soils showed a slight decrease in relative LMW PAH from rural to highly populated areas.

Figure 19 displays the relative share of LMW PAHs at 95% KW & LSD for the three demographic categories excluding values from settlement soils as they will be excluded from seasonal pattern evaluation. However, a distinction between rural and fairly populated areas could be found at 60% LSD level, thus falsifying the zero hypothesis. Still, the first two groups were evaluated together, whereas strong variations from sample distributions in between the two categories will be pointed out.

Means of relative LMW abundance at 95% LSD for the three demographic categories

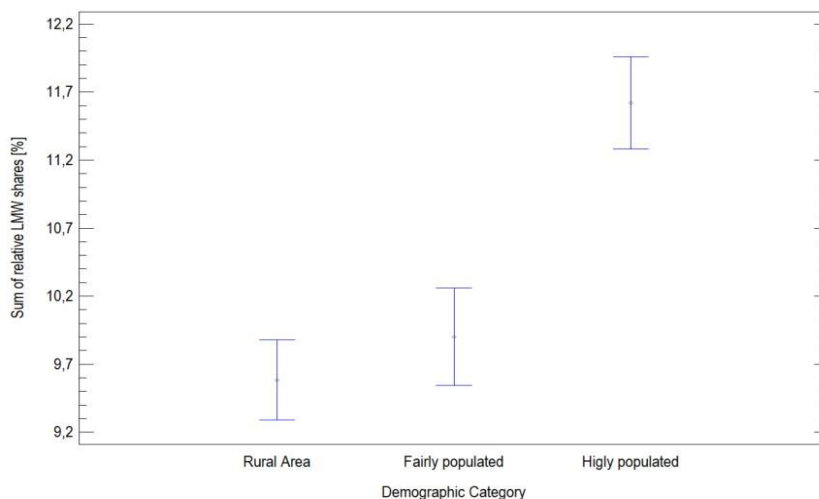


Figure 19: Means of relative LMW abundance at 95% LSD for the three demographic categories

The following results discuss the concentration means of LMW PAHs as well as the relative shares of LMW PAHs in percent. This is because it is expected that LMW shares are more stable in terms of additional LMW input, whereas concentrations are more likely to be governed by demography. LMW PAH shares in figure 19 displayed the lowest values for rural areas, followed by fairly populated areas and highly populated areas displayed much higher shares. It is believed that lowest values are visible in rural areas because these soils are most remote, in terms of the categories discussed, which results in less input and therefore a state closest to pseudo – equilibrium. In fairly populated areas shares are a bit higher. Yet, compared to highly populated areas the amount of LMW PAHs is still low as these soils still experience less input.

As initial PCAs revealed in figure 14, Acenaphthylene does not follow the same accumulation pattern as other LMW PAHs. However, Acy was still evaluated as seasonal dependent compound due to correlation analysis results and the knowledge that the compounds vapor pressure is second highest after Naphthalene. Therefore, it is fair to assume that the compound is subject to temperature dependent evaporation.

Figure 20 displays correlation analysis results for the individual months as well as for all months combined (top row). The data used for the correlation heatmaps excluded settlement soils and highly populated areas as this data will also be excluded for the subsequent seasonal pattern evaluations. All correlations showed high levels of significance (>95% CI).

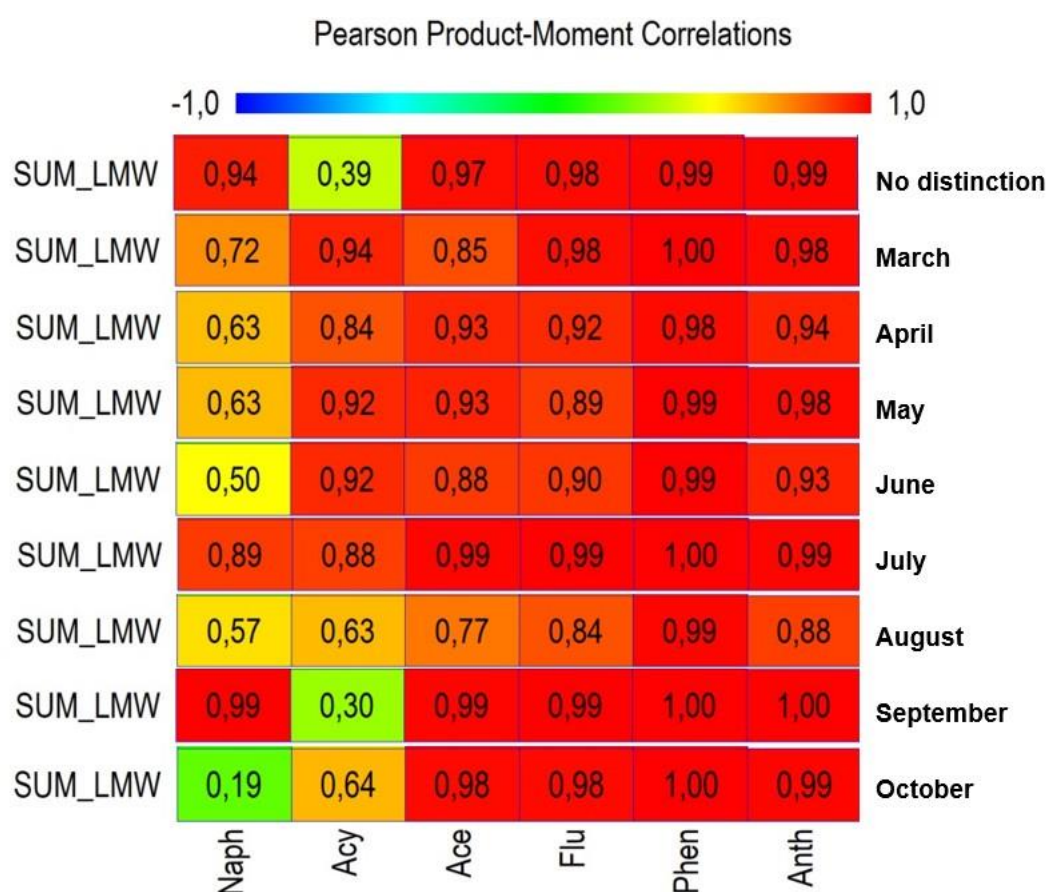


Figure 20: Correlation Heat Map in between the Sum of LMW PAHs and the single compounds for all months and no distinction in between months

Overall correlations for Acenaphthylene seem to be largely based on September results as correlations for other months proved to be of high significance. In fact, overall correlations for Acenaphthylene when September values were excluded, were determined at 0,70. This result then exceeded the one for Naphthalene (0,61).

A multiple X-Y Plot (figure 21) was generated displaying the means of all 6 LMW PAHs and the Sum of LMW PAHs. Again, excluding settlement soils and soils from highly populated areas. Extreme values and outliers were also excluded. As figure 13 indicated, phenanthrene constitutes the most abundant

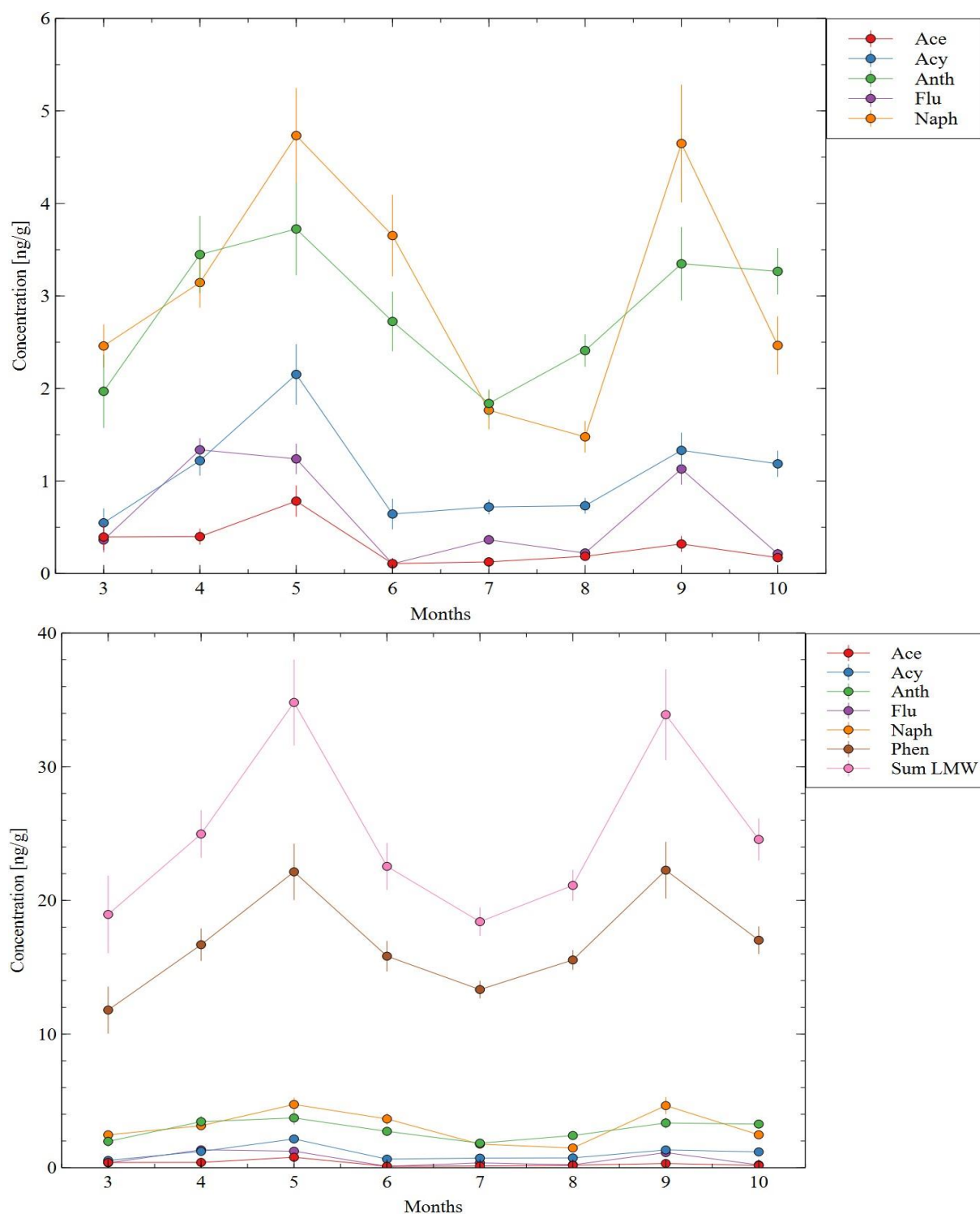


Figure 21: X-Y Plots of LMW PAH means. Top graph: excluding Phenanthrene and Sum LMW for demonstration purposes. Bottom graph: All 6 LMW PAHs and the SUM LMW PAHs.

LMW PAH, therefore the compound strongly governs LMW PAH patterns. This is confirmed by the compound's correlation to the Sum LMW ($>0,99$) for all months.

Yet, correlations between Phenanthrene and the sum LMW PAHs excluding Phenanthrene also showed very high correlations: Mar: 0,96; Apr: 0,87; May: 0,95; Jun: 0,95; Jul: 1,00; Aug: 0,89; Sep: 0,99; Oct: 0,98 & Ø: 0,95. Concomitantly the correlation of Sum PAH including Phenanthrene and Sum PAH excluding Phenanthrene showed correlations $>0,95$ – All values with a level of significance (LS%) above 95%. Therefore, Phenanthrene and Acenaphthylene were included in Sum LMW PAH and seasonal pattern evaluations.

Figure 21 displays the means of all LMW PAHs. The top graph excludes Phenanthrene and Sum LMW for demonstration purposes, whereas the bottom graph includes them. The data combines values of agricultural, grassland and forest soils.

As visible, all compounds show a relevant drop in mean concentrations during June, July and August. However, also March, April and October show lower means for most compounds. This will be discussed in detail for all land use categories within this chapter. Naphthalene as the most volatile representative displays biggest deflections, which is most likely the reason for comparatively little correlation per month towards Sum LMW.

I. Agricultural Soils

Figure 22 shows the results for agricultural soils. The left means plot refers to means of absolute LMW concentrations whereas the right graph shows results for relative shares of LMW PAHs in percent during the time frame assessed. Extreme values as well as outliers were excluded from evaluation. Both evaluations were conducted at 95% LSD and showed a significant difference according to Kruskal Wallis tests at the 95% confidence level.

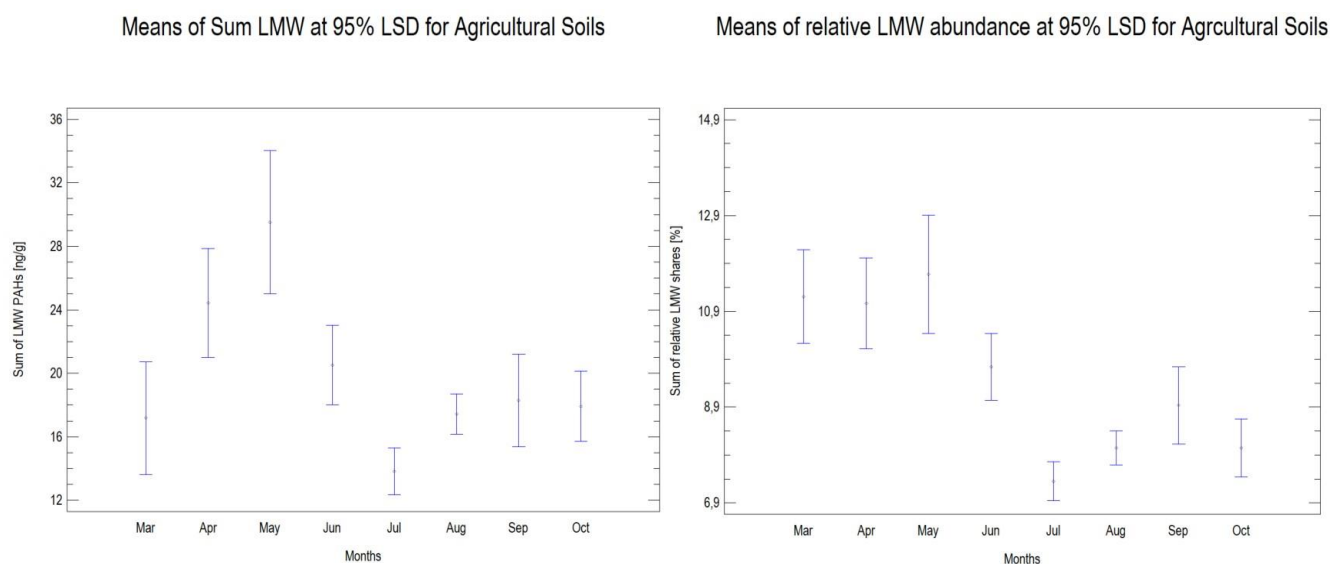


Figure 22: Means of Sum LMW at 95% LSD [left] and Means of relative LMW abundance at 95% LSD for Agricultural Soils [Right]

As visible in the left graph of figure 22 referring to absolute concentration did not display a clear seasonal pattern. Also, the month of May showed very high concentrations in comparison to other months, whereas the relative shares showed no irregularities. This is due to the demographic pattern of the samples taken during this month. 39% of samples were taken in rural, 61% in fairly populated areas. High absolute concentrations in fairly populated areas were not excluded from evaluation as

extreme values and outliers were determined for the individual utilization and demographic categories.

Evaluation of relative abundancies on the other hand displayed a much clearer seasonal pattern. At 95% LSD, March, April and May shares proved to be relatively stable and showed higher values than consecutive months. At 95% LSD, values of May proved to be significantly higher than values for June, as well as March and April and the significance level was found at 90% and 85% LSD.

Also, shares of summer months are significantly lower than values of previous months, followed by a slight increase in September (distinct at 85% LSD) and a decrease in October. Samples in October did show a different pattern than expected. Even though most samples were taken in rural areas (53%), relative shares in rural areas displayed higher values (8,4%) than fairly populated areas, where 7,7% of LMW shares were assessed. Most likely, this is due to PAH input from predominantly HMW PAH containing sources by e.g. wood ovens by the local population, which tilts the balance towards HMW PAHs.

As relative shares dropped from spring to summer months, a rise in values of both concentrations as well as relative amounts of LMW was expected with decreasing temperatures and concomitant reaccumulation in soils. The absence of this phenomenon might be based on land use practices. Agricultural soils are subject to tillage after harvest. Therefore, the soil is suspected to be loose, offering more surface area and is concomitantly more accessible to air, enhancing gas exchange and oxidation by airborne radicals as well as UV impact between soil particles and the vapor phase whereas the lack of vegetation on these soils after harvest, with the missing forest filter effect, makes the accumulation process a sole subject to deposition. As discussed previously, vegetation covers with higher vertical profiles showed higher inputs as the above ground biomass captures airborne PAHs. That is why the lack of vegetation results in a decrease of input. As will be discussed later, agricultural soils also showed lowest amounts of humus and little correlations observed in between humus and LMW PAHs. That may also have an impact on accumulation capacity of these soils for the data in question.

Relative LMW abundance displayed a clear seasonal pattern for LMW PAHs in agricultural soils. However, also absolute concentrations showed similar deflections with smaller changes of values causing results to be of little significance. As values for March and April were lower and those for the month of May higher, no obvious pattern was discernible.

II. Grassland soils

Figure 23 shows the results for grassland soils. The left graph displays the means of absolute LMW concentrations, whereas the right graph shows results for relative shares of LMW PAHs in percent. Both graphs at 60% LSD with a 95% confidence level ($>0,05$) according to Kruskal Wallis tests. Again, extreme values and outliers were excluded from evaluation. LSDs were set to the minimum level of distinction in between summer months (Jul & Aug) and previous as well as consecutive months referring to LMW shares. For direct comparison purposes means of LMW concentrations are displayed at the same LSD value.

Evaluation of grassland soils do not show a clear pattern as agricultural soils do. The samples taken during the months of March and April were mostly governed by rural areas. As for May, 63% of samples

were taken in fairly populated areas, which explains the high absolute values for that month as well as some of the LMW share.

Means of Sum LMW at 60% LSD for Grassland Soils

Means of relative LMW abundance at 60% LSD for Grassland Soils

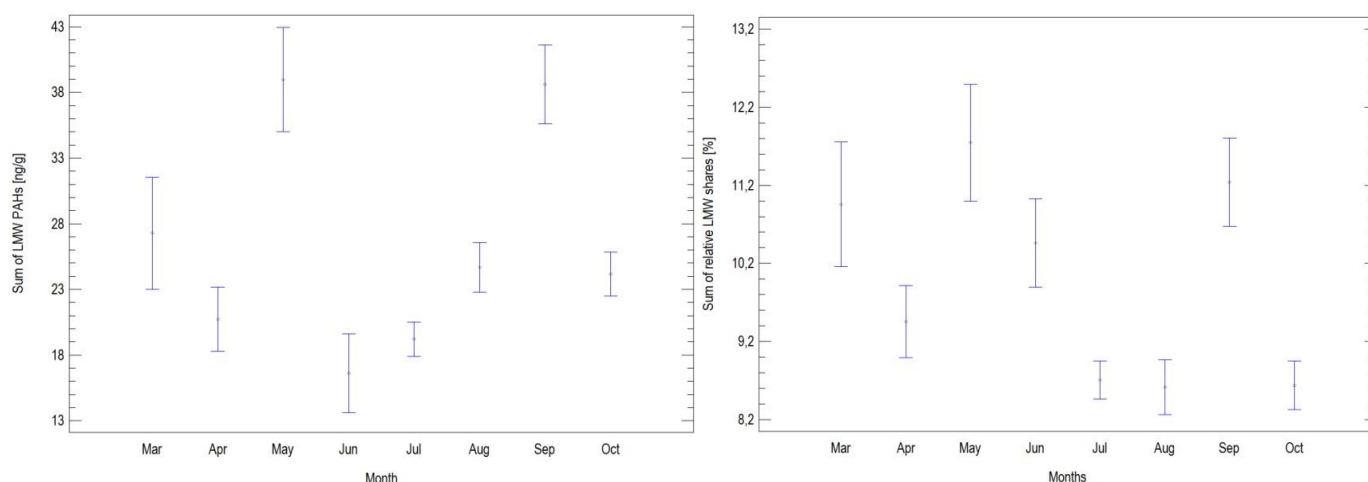


Figure 23: Means of Sum LMW at 60% LSD [left] and Means of relative LMW abundance at 60% LSD for grassland Soils [Right]

However, the same could be said for June, where 64% of samples were taken from fairly populated areas with considerably lower absolute as well as relative LMW values/shares. Yet both months show very different constellations in both graphs. Sampling frequency during July and August was sufficient, though August sampling was mostly conducted (53%) in fairly populated areas, which may explain higher absolute concentrations. As for September, samples were taken mostly in rural areas (57%) which leads to the question where these values come from. A pattern could not be observed. However, 60% LSD was set to show lower relative LMW PAHs shares for summer months.

The answer seems to lie within population density, as figure 24 demonstrates. For demonstration purposes, seasonal evaluation was additionally evaluated for rural areas of grassland soils only. Kruskal Wallis confidence levels were above 95%. As sampling frequency was low, error bars, especially for LMW shares, show high variance.

Means of Sum LMW at 60% LSD for Rural Grassland Soils

Means of relative LMW abundance at 60% LSD for Rural Grassland Soils

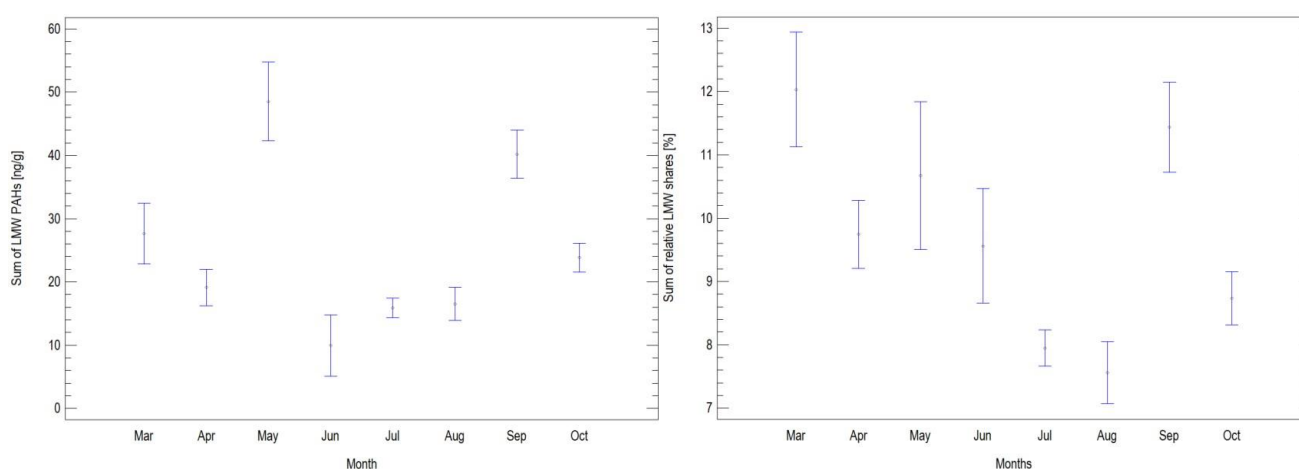


Figure 24: Means of Sum LMW at 60% LSD [left] and Means of relative LMW abundance at 60% LSD for Rural grassland Soils [Right]

Most of the concentration pattern is comparable with what was displayed before (figure 23). Yet, LMW shares achieve to show more of a seasonal pattern. At 60% LSD values of July and August are lower

than previous and consecutive months. Again, October values are surprisingly low which goes along with what was found in overall evaluations (fig. 21) and agricultural soils (fig. 22).

III. Forest soils

Figure 25 shows the results for forest soils. Again, the left plot shows the means of absolute LMW concentrations at 70% LSD and the right plot demonstrates results for relative shares of LMW PAHs in

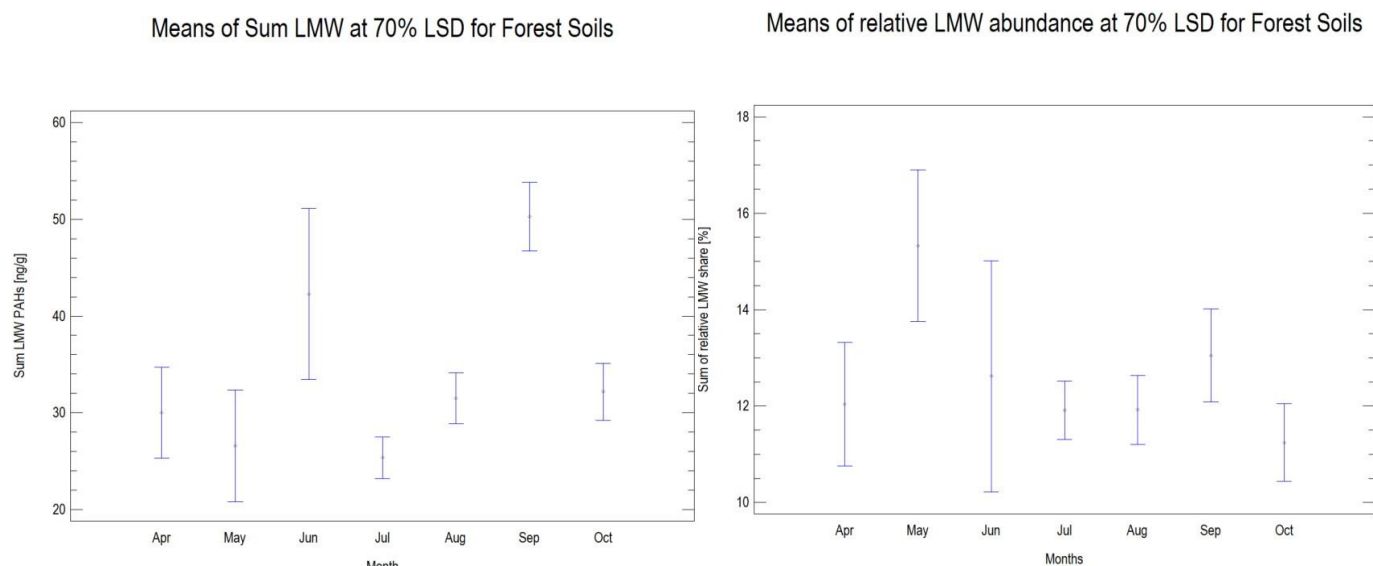


Figure 25: Means of Sum LMW at 70% LSD [left] and Means of relative LMW abundance at 70% LSD for forest Soils [Right]

percent at 70% LSD and KW CI of 95% or above. Extreme values and outliers as well as values for March were excluded because only one sample event took place for forest soils during the whole month.

Also, evaluation of forest soils for both demographic categories showed major irregularities. This is mostly based on what was previously explained for grassland soils. Especially values for June are highly inconsistent - only six samples were taken during that month whereas 67% (4 samples) originated from fairly populated areas. As indicated before, in forest soils relative LMW PAH shares decrease with population density which is also visible in figure 25.

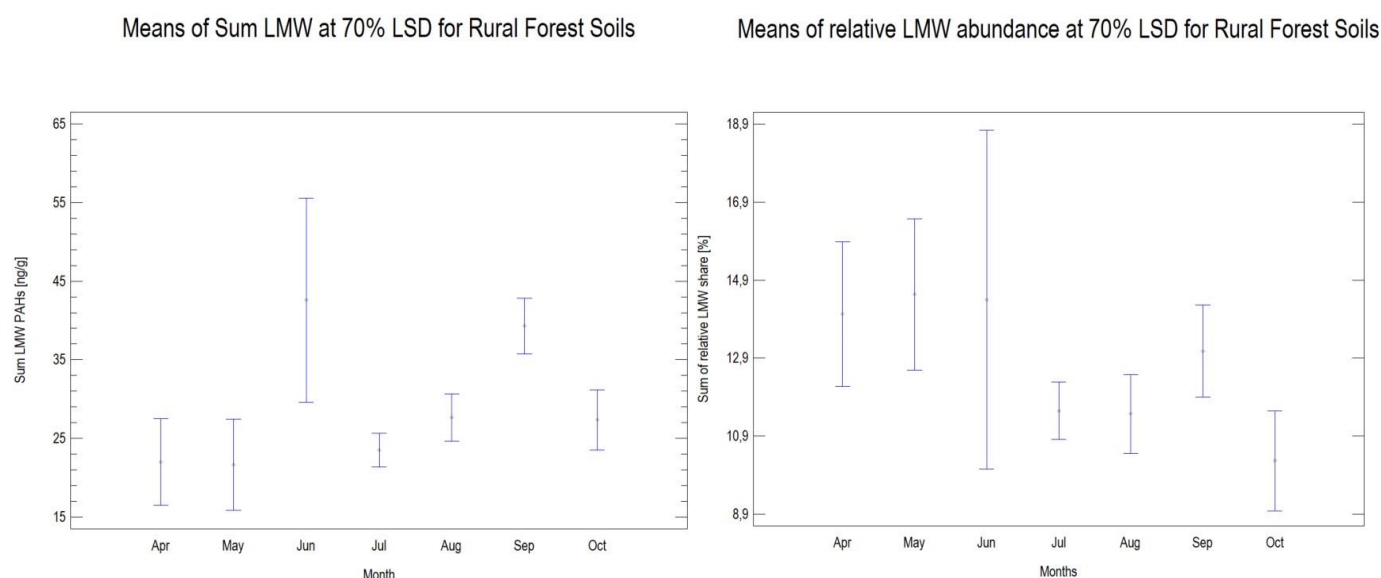


Figure 26: Means of Sum LMW at 70% LSD [left] and Means of relative LMW abundance at 70% LSD for rural forest Soils [Right]

Figure 26 displays differences for rural areas only at 70% LSD. Absolute concentrations do not show much of a difference as compared to the evaluation of both demographic categories. However, results for relative shares differ for the months April and June, resulting in a somewhat clearer pattern. Yet, the result for June is based on 2 samples only, showing in vast error bar extent. Still, at least relative LMW PAH shares display, next to October, lowest values for the warm summer months. Thus, seasonal variation can be confirmed to some extent with emphasis on relative shares rather than absolute concentrations.

In conclusion, all three land use types displayed clearer seasonal variation regarding relative shares than absolute concentrations. This is most likely the case because of a stronger dependency of absolute values on the demographic category. Also, all three land use categories showed lowest LMW PAH shares during summer months. Previous and subsequent months did not always display the expected pattern as clearly. Especially October values of absolute concentrations as well as relative shares for all land use categories proved to be unanticipatedly low.

Results for agricultural soils displayed the pattern clearest, consequently splitting the data into rural and fairly populated areas was unnecessary. However, agricultural soils pose the utilization group sampled most, thus splitting the data for this category would have been an option in case of insignificant results. Whereas, this cannot be said for grassland nor forest soils as sampling proved to be insufficient for various months while others were more frequently sampled. Consequently, splitting the data defeats the purpose of posing an unambiguous statement but was still conducted to clarify some of the results presented. To do so, rural areas were selected as they are expected to represent remoteness and hence seasonal variation, governed mostly by evaporation, better than fairly populated areas with uncertain reoccurring input

IV. The three major conurbations: Dresden, Leipzig and Chemnitz

The three biggest cities of Saxony were further investigated as they showed various features that are worth discussing. First off, daily precipitation values for these three cities did not display a significant difference. For evaluation extreme values and values below 0,1mm were excluded.

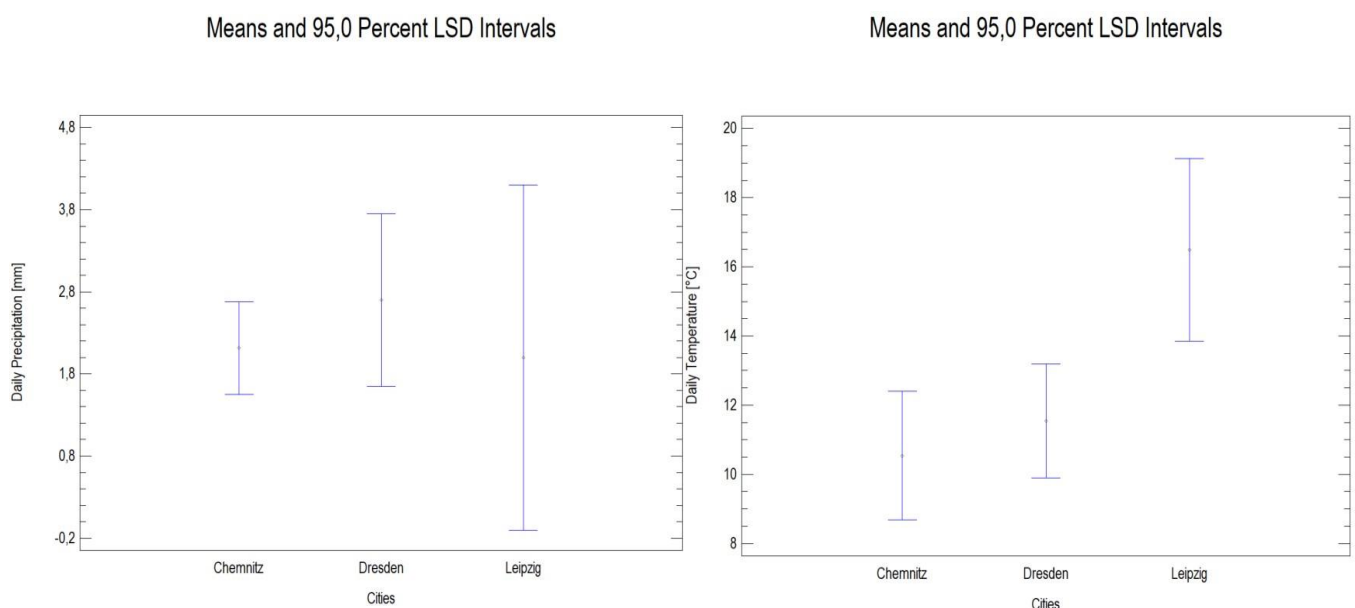


Figure 27: Daily Precipitation means per city in mm [left] and daily temperature means per city in °C [right]

However, daily temperatures in Leipzig proved to be higher than values in Chemnitz or Dresden. A Kruskal Wallis test revealed a significant difference in between the cities at 95% LSD. Means in Chemnitz and Dresden were determined at 10,5 and 11,5°C, whereas in Leipzig the mean temperature was as high as 16,5°C. Figure 27 displays daily precipitation means in millimeters and daily temperature means in degrees Celsius.

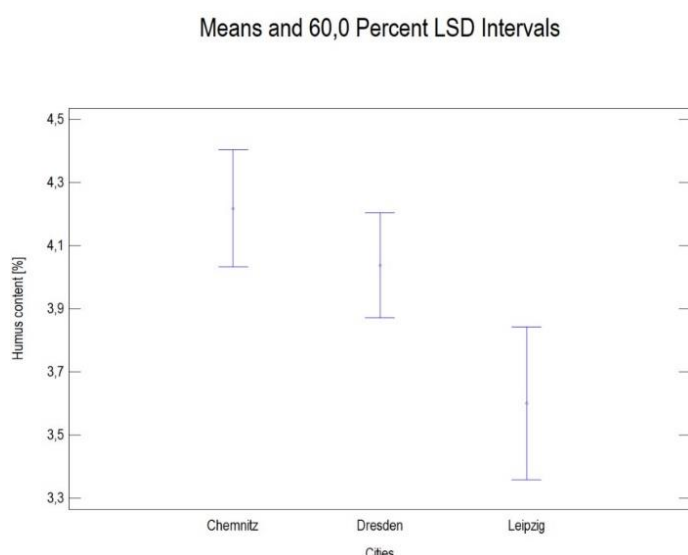


Figure 28: Humus contents in percent of the three cities investigated

Secondly humus contents in these cities were different. Lowest means were found in Leipzig 3,6%, whereas the content was 4,0% in Dresden and 4,2% in Chemnitz. Yet, a Kruskal Wallis test showed that this difference was of minor significance (48%), whereas the post-hoc test, visible in figure 28, showed a difference in between Chemnitz and Leipzig at 75% LSD and in between Dresden and Leipzig at 60% LSD.

As to find out which variable influences PAH distribution stronger, two MANOVAs brought the answer (figure 29). Both used the humus content and the daily temperature as covariates and analyzed the Sum PAH and the sum of low molecular weight PAHs. In both cases humus had more influencing capacities on PAH/LMW PAH concentrations in city soils.

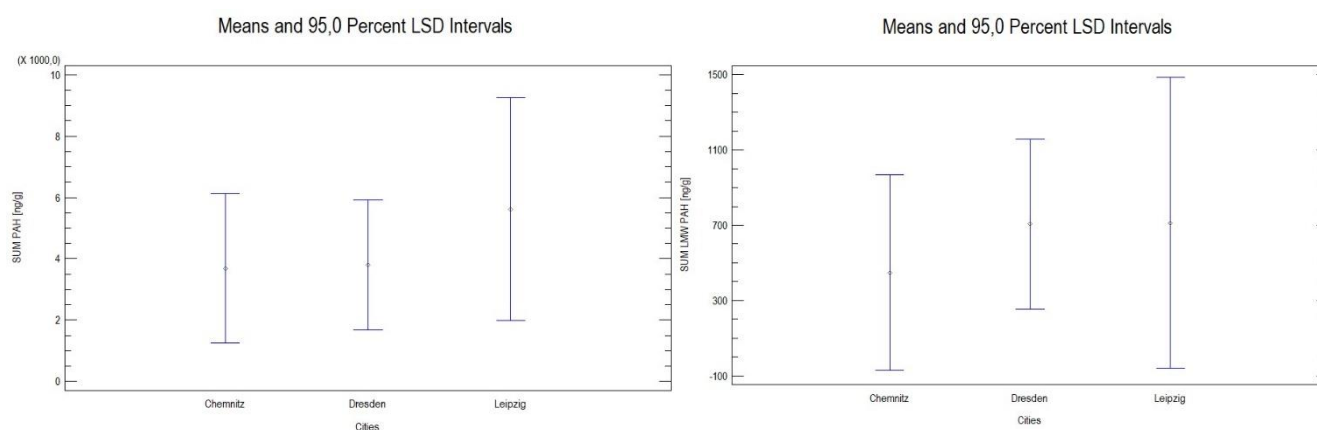


Figure 29: MANOVA results for the Sum PAH [left] and LMW PAHS [right] using humus contents [%] and daily temperature [°C] as covariates

However, in both cases p values were found above 0,05 which indicates that none of the variables had relevant influences on PAH levels. As for the sum PAH humus showed a p-value of 0,165 and daily temperatures of 0,592. As for low molecular weight PAHs p-values were found at 0,357 for humus and 0,611 for daily temperature.

Lastly, the pollution by PAHs was further analyzed. Foremost the overall PAH concentrations, second the LMW PAH concentration and lastly a temperature dependency on naphthalene concentrations. Differences in relative LMW PAH shares were of little significance, wherein means in Chemnitz were found at 11,1% and in Dresden as well as Leipzig at 11,5% with a p-value of 0,72 (KW).

As figure 30 displays, Chemnitz and Leipzig showed greater PAH pollution than Dresden in terms of sum PAH as well as low molecular weight PAHs. As the left graph displays, the difference is greater for sum PAH, with a 55% KW significance at 74% LSD, whereas its 48% KW and 65% LSD for LMW PAHs.

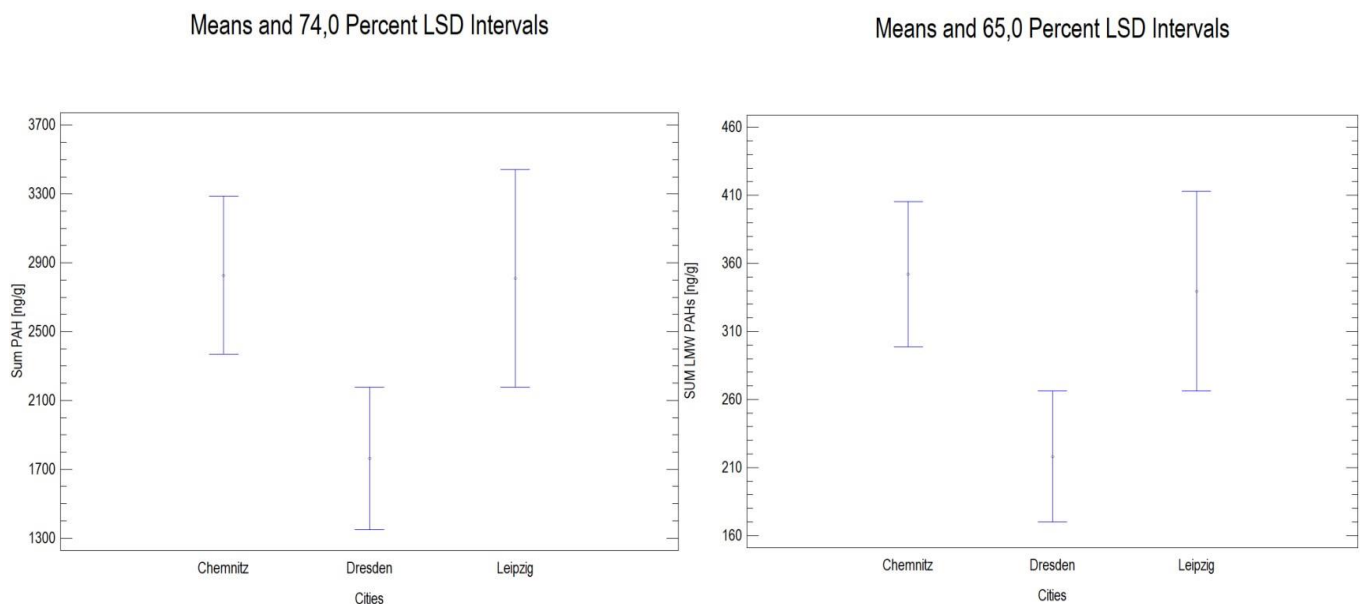


Figure 30: Means of SUM PAH in ng/g [left] and the sum LMW PAH in ng/g [right] of the three cities discussed

Most likely, greater pollution in Leipzig originated from mid Germany's chemical triangle that is located within as well as around the city and is known for the processing of crude oil and chemicals. Chemnitz on the other hand is surrounded by highly populated and industrialized areas, such as the extensively industrialized and inhabited area of Zwickau (and surroundings) –visible in figure 8, map 1 and map 2. Presumably that is the source for higher PAH levels within city borders. Especially compared to Dresden, the extent of highly populated areas and industry is considerable.

Yet, as temperatures were highest in Leipzig, it was expected to find variation in LMW PAHs to some

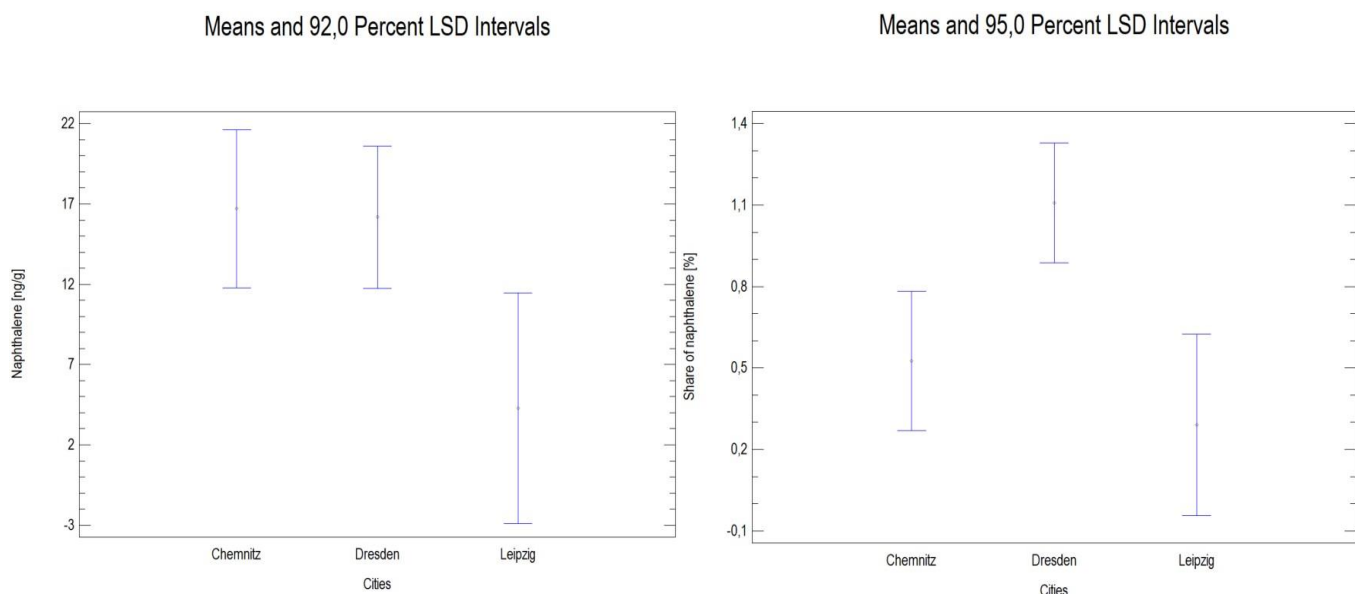


Figure 31: Naphthalene concentrations of the three cities in question [left] and the shares compared to sum PAH [right]

extent. For most LMW PAHs no variation was discernible. However, Naphthalene as the most volatile and susceptible compound to temperature variation displayed a significant difference in absolute

concentrations (KW: 87%) at 92% LSD as well as relative shares (KW: 95%) and 95% LSD (figure 31). Surprisingly absolute numbers for Chemnitz and Dresden were almost identical even though absolute numbers for LMW PAHs were considerably lower in Dresden. Also, relative shares proved to be lowest in Leipzig. The difference at 95% towards Dresden is already significant, whereas a reduction to a 55% significance level was necessary to obtain a discernible difference in between Chemnitz and Leipzig. The difference in between Chemnitz and Dresden is most likely based on general pollution input.

e. Humus categories

First off, it is important to point out that humus contents strongly depend on land use practices. Because humus possesses strong PAH adsorption capacities, this results in different potential PAH adsorption capacities for the distinct land use practices. Agricultural soils show lowest humus contents, followed by grassland soils and settlement soils. Forest soils display highest humus contents. Table 22 displays the number of samples in each humus category and distinguishes in between land use practices. Note that classification for forests is distinct: Humus contents in categories h3, h4 and h5 are higher in forests in terms of percent humus per kilogram of soil.

Humus category	Agriculture		Grassland		Forest		Settlement	
	Abs.	Rel [%]	Abs	Rel [%]	Abs	Rel [%]	Abs	Rel [%]
h0	0	0	0	0	0	0	0	0
h1	4	0,4	0	0	4	0,8	2	0,9
h2	152	14,9	29	7,2	20	3,8	9	4,1
h3	738	72,2	208	51,9	82	15,6	86	39,3
h4	127	12,4	150	37,4	194	37,0	112	51,1
h5	1	0,1	14	3,5	175	28,0	10	4,6
h6	0	0	1	0,2	48	9,2	0	0
h7	0	0	0	0	1	0,2	0	0

Table 22: Absolute and relative numbers for agricultural, grassland, forest and settlement soils of samples divided into humus content categories, based on German pedological guidelines

Humus contents in agricultural soils are most likely lowest because of dilution effects based on tillage and human biomass appropriation. The extracted biomass would otherwise be left on these soils and consequently be reintroduced by decomposition. The high nutrient demand by arable crops is another factor, draining these soils of organic matter and exposing them to external nutrient input. Forest soils are usually found on the other end of the humus content scale – for the purpose of land use categories used in this thesis. This is due to the same reasons. Organic matter on forest soils is left to decompose and thereby increases organic matter content in soils, whereas the top layer is very thin as compared to agricultural soils which results in biomass accumulation. Additionally, lots of biomass is shed by trees and shrub every year in fall. Also, soils in rural settlement areas do often show high humus contents. However, these contents do not originate from natural processes but were artificially translocated for land use management purposes. Humus contents in grassland soils are consequently ranging between agricultural and settlement soils as they are not as highly managed as agricultural or settlement soils which leaves more biomass to decompose. Yet, due to less above ground biomass, less biomass input due to small leave shed and grazing practices by livestock, these values are considerably lower than the ones found in forest soils.

Means and 95,0 Percent LSD Intervals

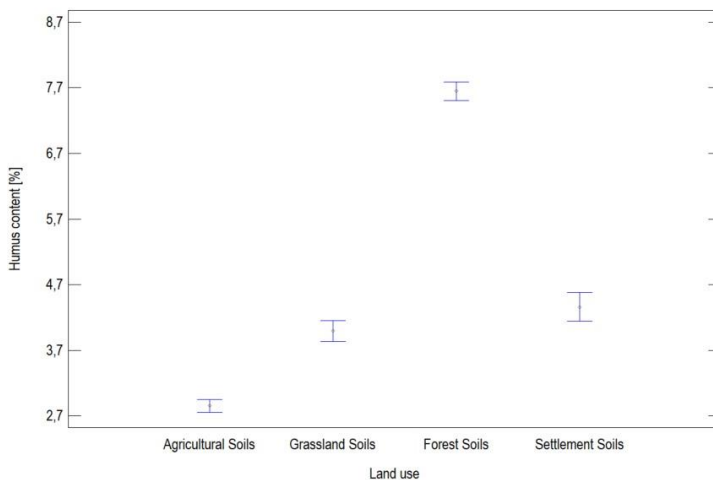


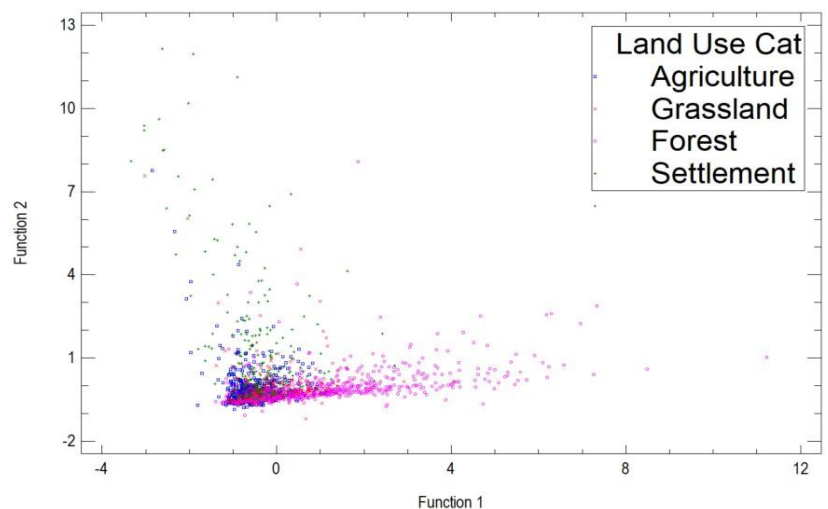
Figure 32: Humus content in percent of the four land use categories

However, a correlation analysis (multiple variable a.) and a discriminant analysis showed, that humus contents correlate stronger to land use than population density. Their distribution in discriminant analysis follows land use functions, wherein two significant functions successfully manage to predict 62% of all cases. The three significant functions for land use categories do predict 37% of all cases only. Discriminant analysis functions are displayed in figure 33 for both, land use as well as demographic categories. The distribution of the data points already shows a much clearer pattern for land use categories than for demography.

To display correlations between the individual PAHs and the humus content data was transformed by using the square roots of absolute concentrations. This is to reduce (right slanted) skewness. However, environmental data, as the data discussed, can't be without significant skew, especially if no categorial differentiation is used for evaluation and the data covers a wide range. As

Figure 32 displays the means and error bars of humus contents in topsoils for the four land use categories discussed within this thesis. At 95% CI by ANOVA, there is a significant difference discernible in between all four groups at 95% LSD. Agricultural soils displayed a mean of 2,9%, grassland soils of 4,0%, forest soils of 7,7% and settlement soils of 4,4%. Demographic categories also showed different humus contents. As different land use categories are predominant in specific demographic groups, a link in between demographic category and humus content can also be detected.

Discriminant Functions by land Use



Discriminant Functions by demography

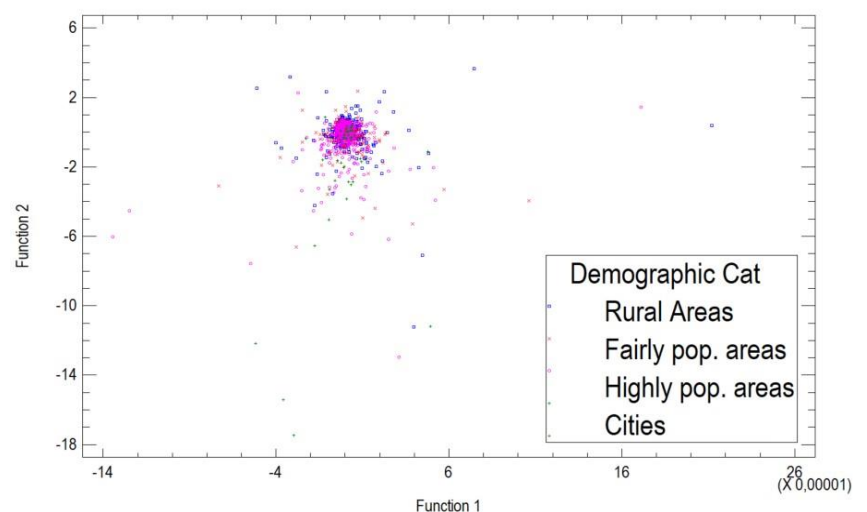


Figure 33: Discriminant functions of Humus and PAHs according to Land Use [top] and demography [bottom]

data transformation will change data distribution shape, PCAs with the variables in question were conducted once with the absolute concentrations and secondly after square root transformation (figure 34).

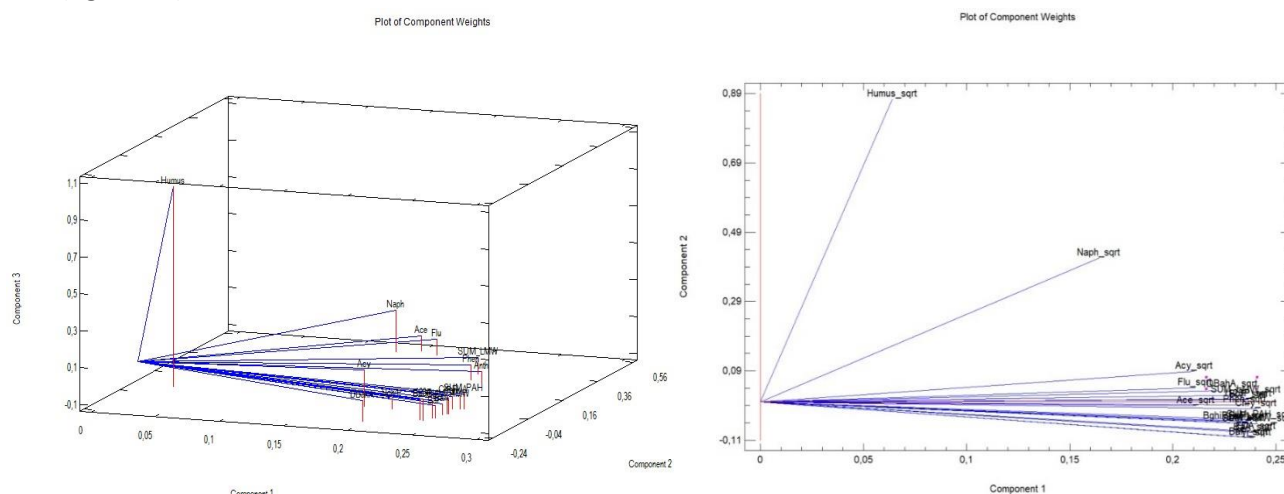


Figure 34: PCAs of the original data including humus [left] and the transformed data [right]

Adding humus to PCA evaluation introduced a third component with an Eigenvalue of 1,0 and an explanatory value of 5% while reducing the variance explained by the previous principal components, that is to say the components without taking humus into account. A MANOVA analyzing the concentration of the sum PAH by demographic category and using humus as covariate, showed that also humus has a statistical significance on PAH distribution, expressed as a p-value of 0,00. (figure 35)

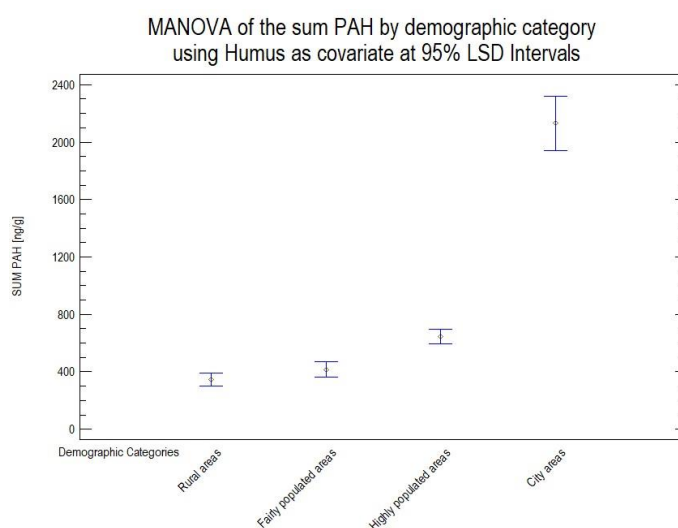


Figure 35: Manova results of the sum PAH by population density & humus as covariate at 95% LSD Intervals

Now, using the square root has three major effects. First: The distribution is reduced to two components, wherein PAHs and humus each account for one component and Naphthalene “stuck” in the middle with significant values for both components, visible in table 23. Second: Standard skewness and kurtosis are greatly reduced. Yet, these values are still over the top with values in between 26 and 53 for standard skewness and in between 20 and 105 for standard kurtosis but compared to prior values in btw. 43 and 621 for standard skewness and 65 and 621 for standard kurtosis. These values refer to samples without group distinction and decrease when groups are singled out as distribution shape changes. Thirdly:

Table of Component Weights

	Component 1	Component 2
Humus_sqrt	0,0639621	0,873556
FluA_sqrt	0,240141	-0,0854471
BbF_sqrt	0,236551	0,00705687
BkF_sqrt	0,236312	-0,0553377
BaP_sqrt	0,236857	-0,102301
BghiP_sqrt	0,225937	-0,0555251
I123P_sqrt	0,236715	0,00854853
Naph_sqrt	0,164003	0,415472
Acy_sqrt	0,210228	0,0884946
Ace_sqrt	0,211045	-0,0109581
Flu_sqrt	0,210753	0,0403877
Phen_sqrt	0,234893	-0,007531
Anth_sqrt	0,23412	-0,0616908
Pyr_sqrt	0,239014	-0,103272
BaA_sqrt	0,238736	-0,0883978
Chry_sqrt	0,240264	-0,0200154
DBahA_sqrt	0,221862	0,0324524
SUM_PAH_sqrt	0,242217	-0,0509372
SUM_LMW_sqrt	0,23528	0,0203561
SUM_HMW_sqrt	0,241091	-0,062136

Table 23: PCA components with square root (sqrt) transformed data set.

Correlation values overall doubled without affecting significance.

Table 24 displays a spearman correlation heatmap in between the square roots (sqrt) of the humus contents, the single PAHs, the sum PAH, the sum of low molecular weight PAHs (SUM LMW) and the sum of high molecular weight PAHs (SUM HMW) at a 95% confidence level. Green tones indicate weak to mediocre correlations, yellow mediocre and orange rather strong correlations. The top row refers to all groups evaluated without differentiation, whereas consecutive rows refer to singled out groups. All land use and demographic categories and interesting combinations of these groups were evaluated individually. Agricultural city soils were added to the plot as they displayed much stronger correlations than agricultural soils on their own. All correlations were highly significant with 95% CI or above. Interestingly high and low molecular weight PAHs do show similar correlations, only a few soil groups, such as forest soils or agricultural settlement soils showed stronger correlations with HMW PAHs.

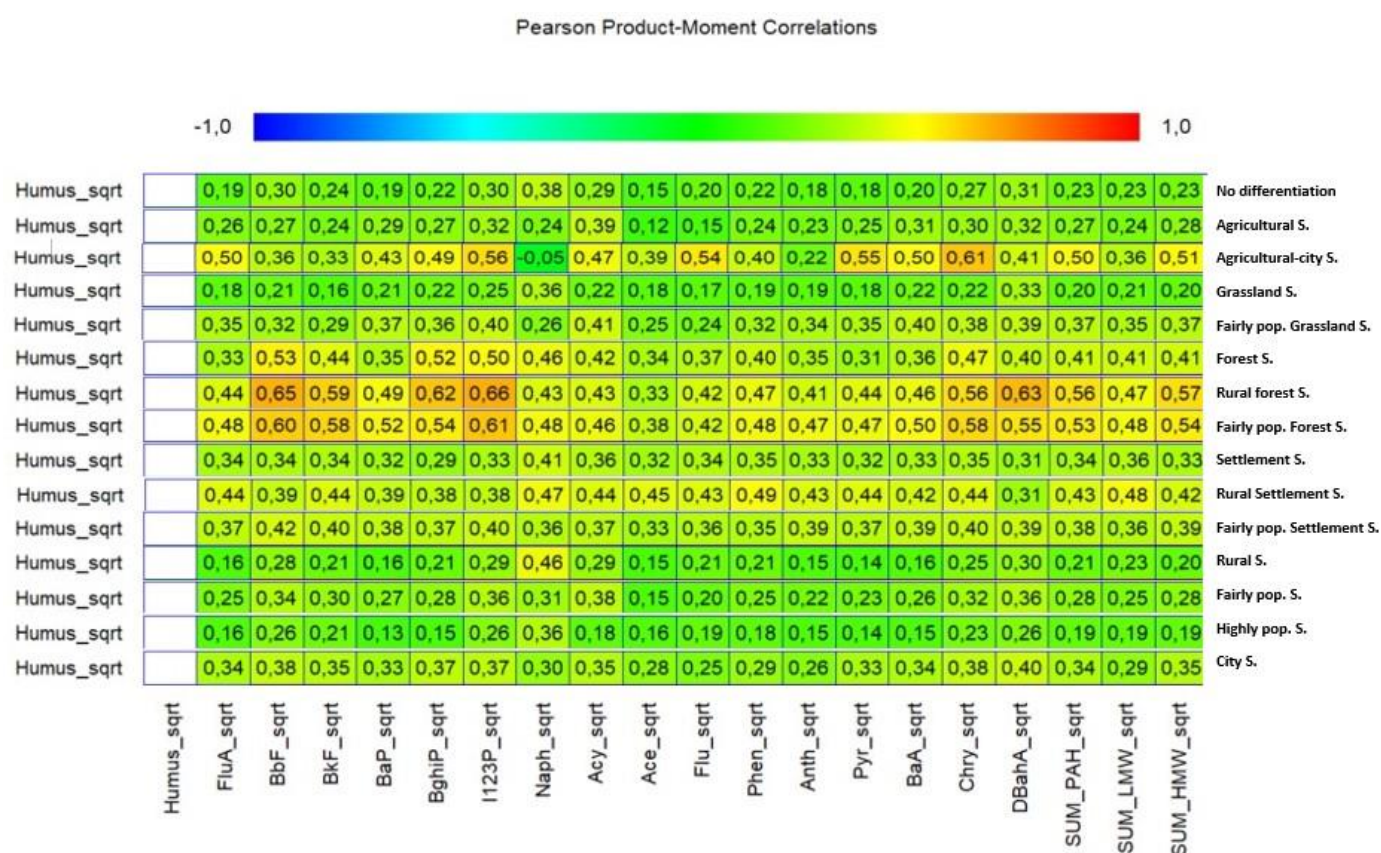


Table 24: Spearman correlations (r) in between the square roots of humus contents, the single PAHs, the sum of PAHs, the sum of low molecular weight PAHs (LMW PAH) and high molecular weight PAHs (HMW PAH) at a confidence level of 95% for all utilization groups as well as the groups on their own. Interesting category combinations were evaluated individually.

Surprisingly enough overall correlations are strongest for Naphthalene, not only for square root values but also for untransformed concentration data. As for the four land use categories, correlations of agricultural soils in between Naphthalene and humus were much lower than for the other categories which is most likely due to land use practices, as elaborated in the chapter “5d seasonal patterns”. Agricultural settlement soils even displayed a slight negative correlation, whereas correlations with most other PAHs are much stronger than for agricultural soils as a whole.

Forest soils on the other hand showed strongest correlations in between the sum of PAHs including LMW as well as HMW PAHs and humus contents. This is also the only group that displayed a clear distinction in between correlations with HMW and LMW PAHs regarding different groups. The two

singled out rural and fairly populated forest soils showed a stronger correlation in between HMW PAHs and humus than correlation in between LMW PAHs and humus.

Forest soils constitute an exception because of what was before explained to be the forest filter effect in the chapter *“3g Degradation, the role of vegetation, sinks and remediation”*. The biomass decomposing on these soils already has strong associations with PAHs that were previously adsorbed on leaf and/or needle surfaces due to their hydrophobic wax coating, whereas different biomass decomposition steps hold distinct amounts of PAHs while associations disband in the process of decay. Moreover, the forest humus type as defined by German pedological classification system has great influence on PAH associations. Mor-humus was found to contain higher levels of PAHs than moder- or mull-humus in previous studies. Yet, the enrichment factors of the three humus types act contrarily. Mull-humus showed the highest, moder medium and mor the lowest enrichment factors. (Lasota and Błońska 2018; Aichner et al. 2015)

Mor-humus or raw humus occurs mostly in acidic soils that contain few microorganisms or animals to decompose organic matter while mull-humus formation is favored by relatively warm and dry climates as well as easily degradable biomass, such as litter derived by deciduous trees. Moder humus is an intermediate between mor and mull humus. So, in a nutshell: During biomass decomposition, the absolute number of PAHs adsorbed decreases, yet the relative amount adsorbed on humus— that is to say the bio concentration factor, increases. This circumstance explains why correlations are higher in forest soils as adsorption is enhanced in these soils due to shear contact with present PAHs. Additionally, it is interesting to see that demography has an impact on correlations when a group (land use) is singled out. Yet, on their own demography seems to have little influencing capacity as correlations are approximately the same and slightly higher values originate from land use predominance.

Rural forest and settlement soils as well as fairly populated forest and settlement soils displayed stronger correlations than the overall forest and settlement group respectively. Vice versa, the other two groups, highly populated and city forest and settlement soils displayed weaker correlations.

In essence, while demography had a high impact on all soils except grassland soils, the patterns are distinct. In agricultural city soils correlations were much higher which is most likely the case due to accessible humus (tillage) and constant PAH input that leads to enhanced adsorption.

In forest and settlement soils remoteness seems to enhance correlations. Yet, it is not as easy to state a definite result for forest soils as results for highly populated forest soils are not much lower than for the general group and only 4 forests in cities were investigated that showed strong negative correlations for all PAHs. Most likely this is the result of large local PAH inputs that skew results. It's much clearer for settlement soils as results are highest in rural soils and decrease towards fairly populated and highly populated soils, latter correlations are quite identical with results from cities.

f. Toxicological assessment

Germany uses the surrogate marker approach using B(a)P as reference substance. Yet, the accuracy of this method has been questioned by various researchers and international organizations, such as the EFSA. Because of that, this chapter assesses the accuracy of this method for Saxon soils. Doing so, toxicological equivalents of B(a)P and the approach suggested by the EFSA will be compared. Furthermore, the amount and distribution of samples exceeding a trigger value of 0,5 mg/kg soil and 1 mg/kg soil will be determined as well as the distribution among results regarding outliers and extreme values. Concentrations above 0,5 mg/kg B(a)P (trigger value for playgrounds) and 1 mg/kg

B(a)P (trigger value for residential areas and agricultural soils) were evaluated. As elaborated in chapter “3f toxicity”, current legislation based on (Bundesministerium der Justiz und für Verbraucherschutz 7/12/1999) provides higher trigger values. However, since states and linking organizations (ALA and LABO) agree that these values were initially set to high and all evidence points to a reduction of these values to the afore mentioned 0,5; 1,0 and 1,5 mg/kg for the different land use categories respectively, this chapter will use latter values as reference.

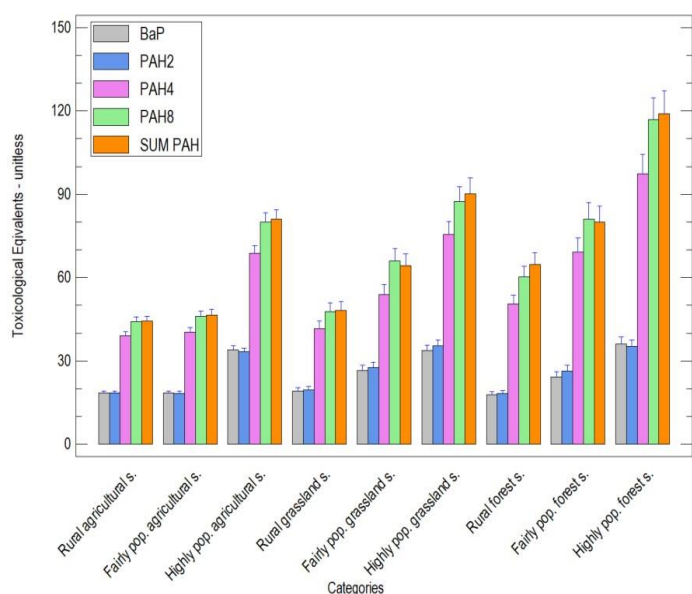
The B(a)P method is an approximation to evaluate total toxicity and is used in Germany according to their decree passed in 1999 (Bundesministerium der Justiz und für Verbraucherschutz 7/12/1999). Yet, according to current standard procedures [DIN ISO 18287 (09/2008)] all 16 US-EPA PAHs are quantified during analysis. This allows a comparison of PAH potencies as described by the EFSA.

Figure 36 and 37 display assessment results and again distinguish in between land use and demographic categories. Listed in the graphs are B(a)P equivalents, the equivalents of PAH2, PAH4 and PAH8 as well as the equivalents for sum PAHs, as suggested by the EFSA. (EFSA 2008)

As the toxicological equivalents are the mathematical product of PAH concentrations and their equivalency factors, the numbers and tendencies equal concentrations for most parts as visible in figure 36. Again, highest toxicological equivalents are found in proximity to anthropogenic PAH sources, rising from rural to densely populated areas as well as from agricultural to settlement soils. Because extreme values and outliers were determined for each variable individually, the sum of toxicological equivalents does not necessarily have to be higher than the sum of PAH8 equivalents. In fact, the sum of PAH equivalents is lower in fairly populated grassland, in rural and fairly populated settlement soils.

As figure 36 shows, absolute values of B(a)P and PAH2 equivalents are fairly similar while the equivalents for PAH4, PAH8 and the sum PAH seem to be comparable. Yet, all 5 equivalents showed a Pearson correlation of 1,0 at a >99,9% CI.

Toxicological equivalents by land use and demographic category



Toxicological equivalents by land use and demographic category

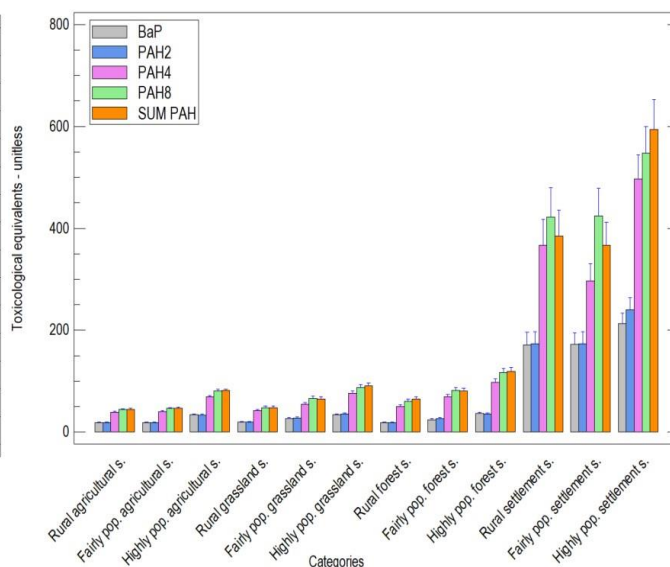


Figure 36: Barchart plot of toxicological equivalents including standard errors by land use and demographic category. For demonstration purposes the left graph shows results excluding settlement soils.

According to a decree published by the Schleswig-Holstein ministry of energy transition, agriculture, environment, nature and digitalization, B(a)P must hold a share of total toxicity in between 30 and 60% for the approximation to be valid. (MLUR 2017) However, this decree refers to soils towards which the population is regularly exposed to and therefore excludes e.g. forest soils. Nonetheless, evaluations include forest soils for comparison purposes and are displayed in figure 37.

Toxicological shares of BaP according to land use and demographic category

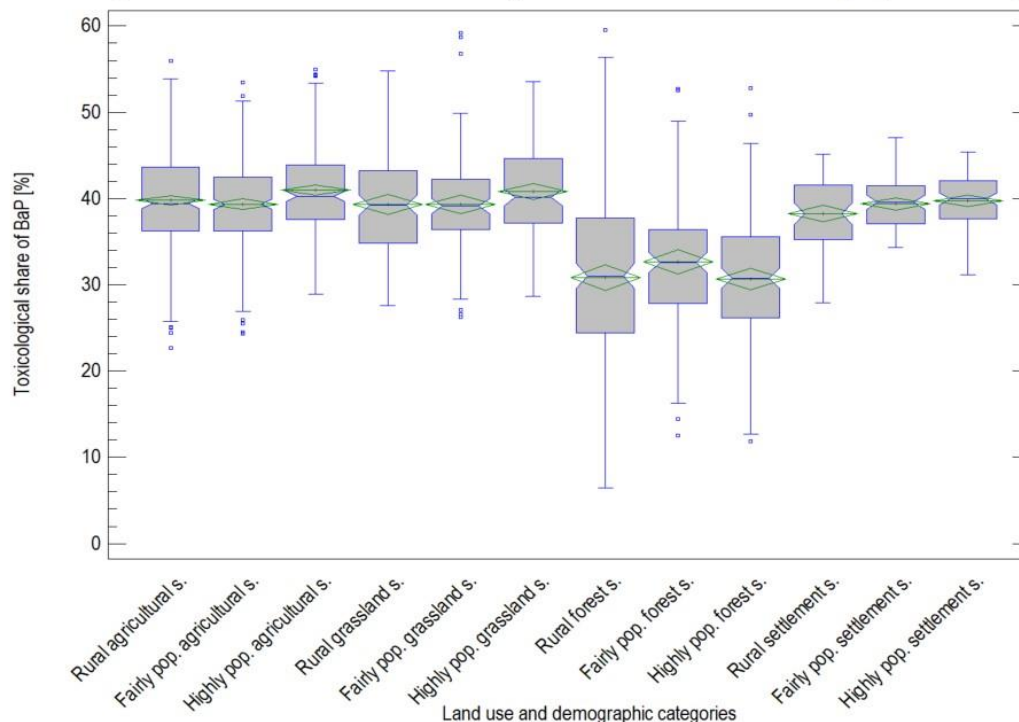


Figure 37: Boxplot of Toxicological Shares of B(a)P by land use and demographic category

Figure 37 serves to display B(a)P shares of toxicity according to land use and demographic category. The upper threshold of 60% is of minor importance, whereas the lower boundary is exceeded more frequently. In agricultural, grassland and settlement soils, exceeds are subject to one-digit numbers, whereas the picture changes completely for forest soils. Means for rural forest soils were determined at 31%, for fairly populated forest soils at 33% and for highly populated forest soils at 31%. Medians showed similar numbers, and both were found just above 50th percentiles. That is to say that 45% of rural forest soils, 43% of fairly populated forest soils and 45% of highly populated forest soil samples were determined to be below the 30% B(a)P equivalent boundary. Now, if the decree was valid for forest soils as well, this result would have major consequences for toxicological evaluations.

Other thresholds within the decree from 2016 include absolute B(a)P concentrations, wherein a threshold of 0,5 mg/kg for playgrounds, 1 mg/kg for residential areas, parks and recreational areas. (MLUR 2016) The input data did not define land use in that sense. That is why an evaluation of both thresholds was conducted, to display both: Threshold exceeds in case results refer to playgrounds, which is rather unlikely and in case concentrations were measured in residential areas, parks or recreational green zones. Results are visible in table 25 and 26.

The threshold of 0,5 mg B(a)P per kilogram soil was exceeded 57 times, whereas 42 exceeds were found in settlement, 2 in forest, 4 in grassland and 8 in agricultural soils. Most of them were determined to be extreme values: 100% in agricultural, grassland and forest soils as well as 31% in settlement soils. In settlement soils, another 29% were found to be outliers. That leaves 17 valid samples (40,5%) exceeding this threshold.

	Agriculture			Grassland			Forest			Settlement		
	All	O	E	All	O	E	All	O	E	All	O	E
Rural	2	0	2	1	0	1	0	0	0	10	0	5
Fairly	3	0	3	1	0	1	1	0	1	13	5	3
Highly	3	0	3	2	0	2	2	0	2	19	7	5
Σ_{total}	8	0	8	4	0	4	3	0	3	42	12	13
$[\%]_{\text{total}}$			100			100			100		28,6	30,9
$[\%]_{\text{valid}}$	0			0			0			40,5		

Table 25: Determination of threshold exceeds (0,5mg/kg) of All samples exceeding the threshold, the number of outliers determined (O) and the number of extreme values determined (E). The total amount of samples taken, and the percentages of total samples determined outliers or extreme values as well as valid samples

Table 26 displays threshold exceeds of 1 mg/kg. Only 25 values were found to exceed this threshold. In 18 cases these exceeds were found in settlement soils, 2 in forest, another 2 in grassland and 3 in agricultural soils. Yet, almost all of them were declared extreme values, with only 5 exceptions in settlement soils that were found to be outliers. That leaves no valid values exceeding this threshold.

	Agriculture			Grassland			Forest			Settlement		
	All	O	E	All	O	E	All	O	E	All	O	E
Rural	1	0	1	1	0	1	0	0	0	5	0	5
Fairly	1	0	1	0	0	0	1	0	1	4	1	3
Highly	1	0	1	1	0	1	1	0	1	9	4	5
Σ_{total}	3	0	3	2	0	2	2	0	2	18	5	13
$[\%]_{\text{total}}$			100			100			100		27,8	72,2
$[\%]_{\text{valid}}$	0			0			0			0		

Table 26: Determination of threshold exceeds (1,0 mg/kg) of All samples exceeding the threshold, the number of outliers determined (O) and the number of extreme values determined (E). The total amount of samples taken, and the percentages of total samples determined outliers or extreme values as well as valid samples

The determination of a sample exceeding the threshold as an outlier or extreme value, does serve to relate high values to general pollution levels. Yet, single trigger value exceedings should be evaluated individually for the necessity of taking measurements.

As last step of the examination cascade for the B(a)P approach to hold is an evaluation of a certain PAH pattern based on shares of B(a)P. Wherein this is expressed as multiples of B(a)P with maximums introduced that are not supposed to be exceeded. Table 27 lists those maximums as "Share of B(a)P" and the number of samples that exceeded these thresholds in absolute numbers as well as percent. The shares for LMW PAHs cover a bigger range than HMW PAHs because they are of minor toxicological importance, which allows the spectrum to be broader without distorting results. It comes as no surprise that none of the volatile PAHs surpassed thresholds as the boundaries are quite high and LMW PAHs were found to be represented by low concentrations only.

Yet, 7 HMW PAHs had at least one sample exceeding the threshold, whereas extreme values and outliers were also evaluated. Low B(a)P concentrations may lead to misinterpretation of threshold exceeds as a multiple (Share of B(a)P) may be surpassed easily. Table 27 distinguishes between shares that were exceeded below and above 5 µg/kg B(a)P. Samples displaying low B(a)P concentrations that exceeded the thresholds were found more frequently. However, a considerable amount of threshold exceeds was also found for moderate B(a)P concentrations. 85 samples were found exceeding the

threshold and displaying a moderate B(a)P concentration, while 94 of them exceeded these thresholds and showed low B(a)P concentrations.

	Share of BaP	Threshold Exceeds		Percent	
		High [BaP]	Low [BaP]		
Naph	160	0		0	
Acy	5	0		0	
Ace	95	0		0	
Flu	110	0		0	
Phen	140	0		0	
Anth	240	0		0	
FluA	55	0		0	
Pyr	30	0		0	
B(a)A	6	0	1	0	
DB(a,h)A	1,5	1	1	0	
Chry	5	10	4	0,5	0,2
B(b)F	3	44	21	2,0	1,0
B(k)F	3	3	16	0,1	0,7
B(ghi)P	3	11	42	0,5	1,9
I(1,2,3-c,d)P	3	16	9	0,7	0,4
Absolute N°		85	94	3,8	4,2
Percent _{Absolute}		3,9	4,3		
Corrected N°		53	48		
Percent _{Corrected}		2,4	2,2		

Table 27: The share of single PAHs (as thresholds) in comparison to B(a)P. The absolute amount of exceeds, the valid number of considered samples and percentage values of exceeds

These numbers refer to the sum of samples found exceeding these thresholds. Some of these samples exceed the threshold for more than one PAH and thereby reduce the absolute number of samples surpassing thresholds considerably. Only 53 samples with moderate and 48 samples with low B(a)P concentrations were found to exceed thresholds. Together they pose 4,6% of all samples taken.

It is safe to state that neither B(a)P concentrations nor thresholds of shares by other PAHs exceed government guidelines relevantly. All B(a)P concentrations above 1 mg/kg soil were found to be extreme values and therefore do not reflect natural background values and the 28 samples found to exceed that threshold pose 1,9% of all samples taken. Again, this reflects general background values but does not imply that measurements are entirely unnecessary regarding the values exceeding these thresholds. Especially since most of them were found in settlement areas where it is safe to presume regular contact of the local population with these soils.

B(a)P-shares of other PAHs are found in less than 5% of all cases which yields in favor of the B(a)P surrogate marker approach for Saxony. The lower boundary of 30% toxicological share by B(a)P was of importance in forest soils only. Since forest soils are excluded from the surrogate marker approach as elaborated, these lower boundary exceedings are irrelevant. Only in scenarios where humans get into contact with these soils on a regular basis it may become relevant (e.g. forests frequently visited for health cures).

An exceeding towards the lower boundary may lead to an underestimation of toxicological potency in these soils as the input data suggests an undervalued toxicological factor. However, as B(a)P thresholds

in these soils were exceeded three times only and these exceeds being outliers, toxicological effects are not expected.

g. Maps of B(a)P and sum PAH

Map 1 and map 2 display B(a)P and sum PAH concentrations graphically. Settlement soils appear as point information and top of layer in these maps. Because concentration in settlement soils strongly exceeds background values, expressed as values of agricultural, grassland and forest soils, these results were set within barriers. Because of the same reasons results for cities were set in barriers as well. City limits were drawn as red lines around the three major conurbations: Leipzig, Dresden and Chemnitz. Highly populated areas are marked with grey lines moving diagonally from the right upper corner to the left lower corner and fairly populated areas are marked with grey dots distributed evenly across these areas. Rural areas remain unmarked.

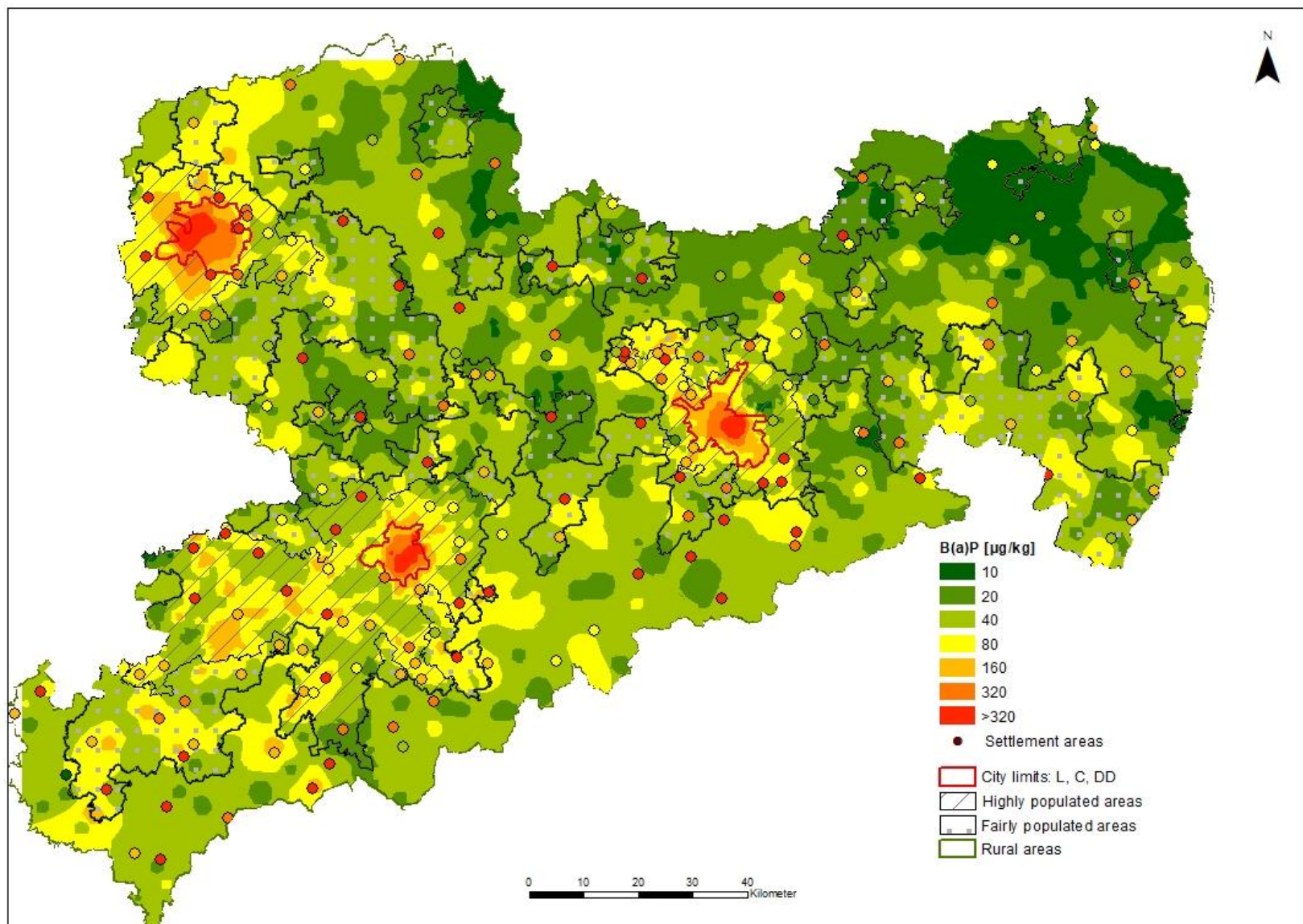
The general trends discussed within the section background values are made visible within these maps. Cities stand out in deep red or orange whereas their surroundings are colored in either orange or yellow. The further away from city borders, the lighter colors get. Orange is found mostly in city surroundings and other conurbations such as Zwickau, Plauen or Reichenbach im Vogtland. This becomes clear when the area marked as “highly populated” is being looked at in detail, as these areas are found exclusively around the three conurbations and a south-western extension of Chemnitz.

The B(a)P map for fairly populated and rural areas is mostly found in the green continuum with some parts colored in yellow. Rural areas additionally show a tendency towards darker green colors as they are more remote. Yet the map for sum PAH shows a greater extent for areas colored in yellow. This especially true for the area between the states south-western border and the highly populated area located around Chemnitz. But also, other areas are affected such as the border region towards Poland and Czech Republic. These areas, including areas across the borders towards Poland and Czech Republic, are very little populated, located at higher elevations and mostly covered by forests. Forests might explain some of the elevated values as background value evaluation showed to be elevated in forests compared to agricultural or grassland soils.

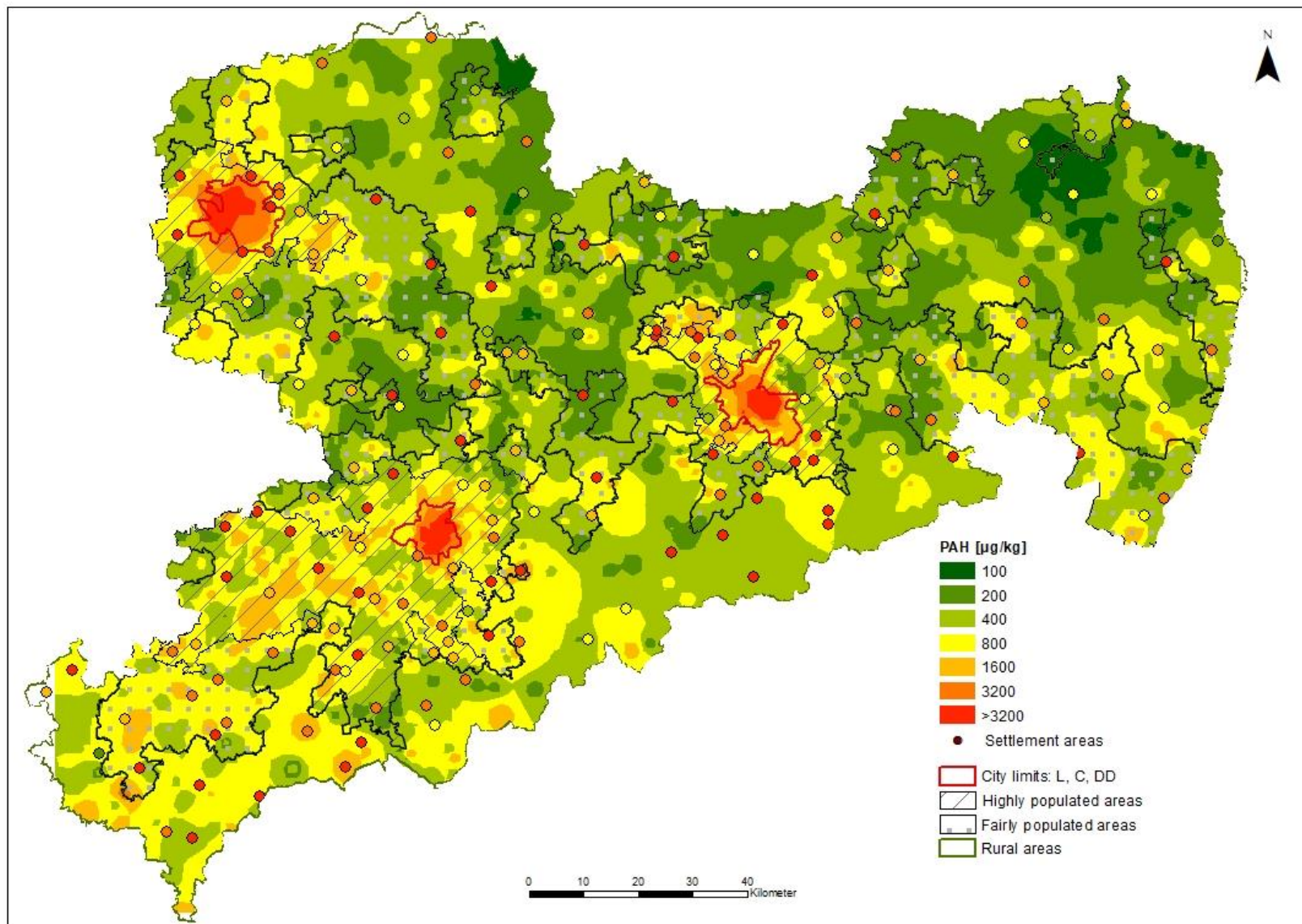
The subdivision of values into colors codes was assumed according to previous PAH maps made by the Saxon State office. The color codes are not based on percentiles, as these maps looked quite uniform and were mostly colored in green. Accordingly, percentile categorization proved to be impractical for demonstration purposes with regards to these maps.

Yet, the color codes of B(a)P concentrations were set to 10% of sum PAH concentrations. Because of that, same colors in both maps indicate that B(a)P concentrations are roughly one tenth of sum PAH concentrations. Correspondingly lighter colors in the B(a)P map indicate a share below 10% and darker colors a share above 10%. As visible for most parts the maps show quite similar colors. However, zones of darker colors are almost exclusively found in the sum PAH map being synonymous with higher concentrations.

Different coloring in the two maps indicate distinct B(a)P/PAH profiles and are most likely found due to distinct PAH input. City soils undergo continuous input which is most likely the reason for the almost identical color codes in both maps for these regions. The further away from densely populated areas (e.g. rural areas) color coding shifts towards lighter colors in the B(a)P map as compared to the sum PAH map (e.g. Saxony's north-western border towards Poland and southern border towards Czech Republic).



Map 1: B(a)P concentration in the free State of Saxony.



Map 2: Sum of PAH concentration in the free State of Saxony

6. Recommendations for future work

Several things are advisable that can help simplify, enhance and extend future situation analysis. Please note, that the suggestions made are based on the evaluations and therefore the posed questions revised in this thesis. In other words: The research questions constitute the basis for the recommendations listed hereafter and therefore different research questions would have most likely led to distinct recommendations. Now, a couple of suggestions will be listed here, and short explanations as of why they are considered important will be given. These suggestions are neither complete nor pressing. However, future work might profit from them if implemented.

First off, it would be advisable to record additional variables, such as daily temperature and daily precipitation during soil sampling. Also, it would be possible to add mean daily temperature and precipitation retrospectively as approximation from the German weather services. These variables are paramount to thoroughly investigate PAH distribution and behavior within the catchment area. It is well known that many PAHs respond strongly to changes of these parameters. Yet, the quality of these responses is subject to these (and other) parameters that set a variety of complex interactions in motion. A deeper understanding and therefore a thorough investigation as well as evaluation of these interactions will profit tremendously from knowledge of these variables.

Furthermore, the amount and distribution of samples strongly influence the data set's exploration capacity. For example: if seasonal variations were of particular interest, it would be advisable to intensively sample soils that are suspected to respond strongest to these variations – city soils. In that sense it is important to know that Saxony has three major conurbations located on different elevations: Chemnitz city center: 297m (highest elevation: 524m), Dresden city center: 201m (highest elevation: 384m) and Leipzig city center: 113m (highest elevation: 181m). (Statistik Sachsen 2019a) This is why the state of Saxony holds large research capacities for explaining climate dependent PAH variation. Additionally, evenly distributed sampling events in terms of sampling events per time interval would allow conclusions about (re)evaporation kinetics and improve the quality of seasonal variation statements. The evaluation presented previously is based on few samples only, whereas the temperature and precipitation results may not generally represent the cities climates but the specific – few – locations where measurements were taken. In other words, the data set used for explanation provided sufficient data to make statements, yet deeper insight would be possible with more samples taken in certain intervals, in terms of higher frequency and over several months.

Another important thought for improving geographical information, that is to say converting point information to surface information, is the spatial distance from one sample point to the next. As figure 9 showed, sampling points used for mapping are unevenly distributed - because of that several issues arise. First, minimum interpolation distances need to be set to the largest distance in between two points of direct vicinity. This distance needs to be rather large if samples are far from each other and even then, interpolation creates sharp divides when few points are considered. Second, if the interpolation distance is high, the points taken into account need to be reduced because of areas of high sampling frequency. If not, results suffer as high and low values would even each other out resulting in a unitary spatial information while in fact a high resolution lies underneath. As alternative, mapping different regions (i.e. districts) with different parameters would be possible. However, this approach may imply misplaced accuracy for regions of little sampling frequency. To avoid that, it is of importance to create a sampling network including a maximum sampling distance so that a minimum resolution is guaranteed. The higher the sampling density, the better the resolution. However, a

network of 3x3km would be advantageous, wherein no sampling location is further than 3 kilometers from the next. These sampling locations refer to agricultural, grassland and forest soils, as settlement soils are excluded from mapping background values anyways and are highly depending on the sampling location.

Also, introducing a unitary sampling practice/guideline that prevents or at least mitigates possible outgassing of volatile PAHs from soil samples is highly recommendable. Also, it would be interesting to compare PAH contents in soils of samples taken as it is currently practiced and if preventing outgassing is emphasized. Even though no papers about (re)evaporation kinetics have been published yet, results of more general papers suggest rather fast temperature responses, in terms of hours to days. (Smith et al. 2001; Tremolada et al. 2009)

So far, suggestions involved mainly sampling guidelines, locations, times and variable recording practices. These suggestions are fairly easy to implement as they do not require additional expenditure but logistics and planning. However, also more principal and even more important - regional research is of interest as causal relationships are often well known but highly depending on local conditions. For example: Investigations of PAH degradation processes (e.g. oxidation by radicals in the vapor phase or photodegradation) might be of importance for especially exposed soils like bare agricultural soils after harvest. Specific metabolization rates by local fungi and plants, field experiments like adsorption onto leaf surfaces of Saxony's vegetation/forests (diversity dependent), evidence of PAHs in ground water and PAH emission models would most certainly contribute a better understanding of the complex processes underlying PAH distribution, mobility and fate.

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