# Atmogenic pollutants as reactive tracers for identification and quantification of important transport processes in a karst area at the catchment scale

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*Für meine Eltern*

# Kurzfassung

Die Zielsetzung dieser Arbeit war es herauszuarbeiten, welche Prozesse langfristig für den Verbleib persistenter organischer Verbindungen im Boden und für deren Transport ins Grundwasser im Feldmaßstab relevant sind. Dazu wurden Vertreter aus der Gruppe der polyzyklischen aromatischen Kohlenwasserstoffe (PAK) ausgewählt, die in verhältnismäßig hohen Raten und flächenhaft durch die atmosphärische Deposition in Oberböden eingetragen werden und den verschiedensten Prozessen im Untergrund (Ad-/Desorption, Bioabbau, partikelgetragener Transport, "preferential flow", etc.) unterliegen. Die PAK stellen damit reaktive und im Einzugsgebietsmaßstab räumlich integrierende Tracer dar, die es erlauben, die transportrelevanten Prozesse zu identifizieren und zu quantifizieren.

Ein geeignetes Karsteinzugsgebiet (Schwäbische Alb, Blautopf) wurde ausgewählt, in dem eine zuverlässige Eintrags- und Austragsmassenbilanz erstellt werden kann und welches zusätzlich erlaubt, Fragen zur Verletzlichkeit und Gefährdung von Karstgrundwässern zu beantworten. Der Eintrag in das Einzugsgebiet erfolgt über die atmosphärische Deposition, die eine sehr konstante Rate über das gesamte Einzugsgebiet aufweist. Es lassen sich jahreszeitlich bedingte Schwankungen nachweisen, mit höheren Werten im Winterhalbjahr.

Böden beinhalten das größte Schadstoffinventar und stellen somit einen wichtigen Faktor dar, um die Speicherung und den Transport von PAK zu quantifizieren. Über das Verteilungsmuster kann ausgesagt werden, dass der Eintrag nahezu ausschließlich über die atmosphärische Deposition erfolgt.

Im Sickerwasser, das direkt in den Höhlen, sozusagen in-situ, beprobt wird, werden unter "normalen" Fließbedingungen nur sehr niedrige oder gar keine PAK-Konzentrationen gemessen. Diese geringe Mobilisierung konnte im Elutionsversuch im Labor bestätig werden. Bei Schneeschmelzen steigen die Konzentrationen sprunghaft an und übersteigen zum Teil den Grenzwert für Benz(a)pyren (BaP). Diese Ergebnisse lassen sich in den Untersuchungen im Grundwasser wieder finden. Im Blautopf korreliert die zunehmende PAK-Konzentration mit der zunehmenden Schüttung und der Turbidität. Die Korrelation zeigt, dass der Haupttransportmechanismus von PAK mit Partikeln verbunden ist. Es konnte nicht gezeigt werden, ob die Partikel direkt von der Oberfläche kommen oder resuspendiert werden. Um die niedrigen Konzentrationen im Wasser messen zu können, wurde ein zeitintegrierendes Messsystem entwickelt. Dieses bewährt sich für die Bestimmung von Hintergrundwerten, kann aber einzelne Ereignisse (z.B. Schneeschmelze), nicht auftrennen und somit muss hierfür die konventionelle Wasserprobennahme eingesetzt werden.

Die Eintrags-/Austragsmassenbilanz zeigt, dass 90 % der PAK im System verbleiben. Davon werden mehr als 50 % mit Ereignissen ausgetragen. Die PAK reichern sich in den Oberböden an und werden nicht mit dem Grundwasser aus dem Karstsystem ausgetragen.

Um die Vorgänge im Untergrund besser verstehen zu können, wurden zusätzlich stabile Isotopen im Wasser untersucht. Das sich jahreszeitlich verändernde isotopische Signal des Niederschlages konnte weder im Sicker- noch im Grundwasser nachgewiesen werden. Dies zeigt eine vollständige Durchmischung und Speicherung des Sickerwassers in der vadosen Zone an.

# Abstract

The aim of this work was to find out which processes are relevant for the fate and transport of persistent organic pollutants POPs in field scale. Therefore, polycyclic aromatic hydrocarbons (PAHs) were chosen, because they are ubiquitous and have a lateral high input rate via atmospheric deposition. They undergo different processes as ad/-desorption, biodegradation, particle-associated transport and preferential flow. Thus, PAHs are reactive and space integrating tracers, which allow identifying and quantifying transport processes.

A suitable karst system (Blautopf Catchment) was chosen, for which a reliable input/output mass balance can be established. Additionally, it is possible to answer questions considering the vulnerability of (karst) groundwater. The input into the catchment happens via atmospheric deposition, which shows a stable deposition rate over the whole catchment. Seasonal fluctuations can be detected with higher values during winter.

Soils have the largest storage capacity for contaminants. Thus, they are a main factor to quantify the storage and transport processes of PAHs. The distribution patterns show that the atmospheric deposition is responsible for the input.

In the seepage water, which is directly sampled in the caves, there are only low or even no concentrations of PAHs during "normal" flow conditions. This low mobilisation could be verified in the laboratory with leaching tests. During snowmelts the concentrations jumped up and exceeded the limit for benz(a)pyrene BaP in drinking water. These results can also be found in the groundwater. In the Blautopf Spring the increasing concentrations of PAHs correlated with the increasing discharge and the turbidity. This correlation shows that the main transport process is linked with particles. It could not be identified if the particles are from the surface or if they have been resuspended in the system. A time integrating sampler was developed to measure the low concentrations of PAHs in the water. This sampling device is proved for background concentrations. However, it is still necessary to use the conventional water sampling for high flow events, as snowmelts or heavy rain events.

The input/output mass balance shows that 90 % of the PAHs remain in the system. Of these more than 50 % can be associated with high flow events. PAHs accumulate in the top soils and do not get transported out of the karst system.

To understand the processes in the subsurface stable isotopes were investigated. However, the changing isotope signal of the precipitation could not be detected in the seepage and groundwater. This shows a complete mixing and storage of the seepage water in the vadose zone.

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# Nomenclature

| **Abbreviation** | **Commentary** | **Unit** |
|---|---|---|
| ASE | accelerated solvent extractor | |
| BBodSchV | Bundes Boden Schutz Verordnung (Soil Protection Decree) | |
| DIN | Deutsches Institut für Normung (German Institute for Standardisation) | |
| DOC | dissolved organic carbon | |
| DOM | dissolved organic matter | |
| FNU | Formacin Nephelometric Unit (turbidity) | |
| HMW-PAHs | high molecular PAHs (BbF-DahA) | |
| HOCs | hydrophobic organic compounds | |
| IRA | used adsorber material, IRA Amberlite 743 | |
| LMW-PAHs | low molecular PAHs (Any-Phe) | |
| n.d. | not detected | |
| OM | organic matter | |
| PAHs | polycyclic aromatic hydrocarbons | |
| POPs | persitent organic pollutants | |
| PTFE | teflone | |
| PVC | polyvenylchlorid | |
| SV | column test (Säulenversuch) | |
| SVOCs | semi-volatile organic compounds | |
| TIC | total inorganic carbon content | $[M\ L^{-3}]$ |
| TIpS | time integrated passive sampler | |
| TOC | total organic carbon content | $[M\ L^{-3}]$ |

**List of the used symbols with units:** M = mass, L = length, $L^3$ = volume, t = time

| | | |
|---|---|---|
| 1/n | Freundlich exponent | [-] |
| a | constant | [-] |
| $A_s$ | area | $[L^2]$ |
| b | constant | [-] |
| $C_{c,tv}$ | threshold concentration in the soil | $[M\ L^{-3}]$ |

| | | |
|---|---|---|
| $C_{org}$ | content of organic carbon | [%] |
| $C_s$ | concentration sorbed onto solids | [M M$^{-1}$] |
| $C_{s,act}$ | actual concentration in the soil | [M M$^{-1}$] |
| $C_w$ | solute concentration in water | [M L$^{-3}$] |
| $C_{w,m}$ | measured aqueous concentration | [M M$^{3}$] |
| D | deposition rate | [M L$^{-2}$ t$^{-1}$] |
| d | depth of the soil | [L] |
| Du | duration of the total contaminant output | [t] |
| E | enrichment factor | [-] |
| F | flux | [M t$^{-1}$] |
| $f_{oc}$ | fraction of organic carbon | [-] |
| $I_c$ | bulk atmospheric input into the catchment area | [M] |
| Inv | inventory of PAHs in soils | [M L$^{-2}$] |
| $K_{oa}$ | octanol-air partition coefficient | [-] |
| $K_d$ | distribution coefficient | [L$^{3}$ M$^{-1}$] |
| $K_{Fr}$ | Freundlich sorption coefficient | [L$^{3}$ M$^{-1}$] |
| $K_{Fr}^*$ | solubility normalised freundlich sorption coefficient | [L$^{3}$ M$^{-1}$] |
| $K_{oc}$ | organic carbon based distribution coefficient | [L$^{3}$ M$^{-1}$] |
| $K_{oc}^*$ | solubility based organic carbon based distribution coefficient | [L$^{3}$ M$^{-1}$] |
| $K_{ow}$ | octanol-water partitioning coefficient | [-] |
| L | water discharge in the column | [L$^{3}$ t$^{-1}$] |
| M | amount of contaminants in the soil | [M] |
| $m_d$ | mass of dry sample | [M] |
| $m_w$ | mass of water | [M] |
| n | number of days | [t] |
| $O_c$ | output of the catchment | [M] |
| Q | average discharge of the spring | [M$^{3}$ t$^{-1}$] |
| R | universal gas constant | [kJ K$^{-1}$ mol$^{-1}$] |
| $r^2$ | correlation coefficient | [-] |
| SL | suspended load in the spring | [M] |
| $S_{sub}$ | subcooled liquid solubility | [mol L$^{-3}$] |
| t | temperature | [K] |
| T | turbidity | [NTU] |
| $t_{tv}$ | time to reach the threshold concentration | [t] |
| $V_w$ | volume of water in batch vial | [L$^{3}$] |
| $X_{tot}$ | total sorbate mass in the batch experiment | [M] |
| $X_w$ | dissolved sorbate mass in water | [M] |
| $\Delta H_{Des}$ | molar heat of desorption | [kJ mol$^{-1}$] |
| $\rho_B$ | bulk density | [M L$^{-3}$] |

**Isotopes**

| | | |
|---|---|---|
| $C_t$ | $\delta^{18}O$ signal of the precipitation water | [‰] |
| $C_w$ | weighted mean isotopic composition of the rain water | [‰] |
| LMWL | local meteoric water line | |
| $Q_p$ | annual mean discharge | [L$^{3}$ a$^{-1}$] |
| $Q_t$ | rain amount | [L$^{3}$ M$^{-2}$] |
| R | ratio $^{18}O/^{16}O$ or $^{2}H/^{1}H$ | [-] |
| $t_p$ | mean transit time in the karst aquifer | [t] |
| Vp | void volume of a karst system | [L$^{3}$] |

### Greek symbols

| | | |
|---|---|---|
| $\omega$ | water content | [%] |
| $\chi$ | mean annual deposition | [M $L^{-2}$ $t^{-1}$] |
| $\Phi_{s,ot,f}$ | daily deposition flux | [M $L^{-2}$ $t^{-1}$] |

### Isotopes

| | | |
|---|---|---|
| $\Delta$ | standard deviation | [%] |
| $\delta$ | isotope ratio | [‰] |

### Substances

| | |
|---|---|
| Ace | acenaphthene |
| Ant | anthracene |
| Any | acenaphthylene |
| BaA | benz(a)anthracene |
| BaP | benz(a)pyrene |
| BbF | benz(b)fluoranthene |
| BeP | benz(e)pyrene |
| BghiP | benz(g,h,i)perylene |
| BkF | benz(k)fluoranthene |
| Chr | chrysene |
| DahA | dibenz[a,h]anthracene |
| Fln | fluorene |
| Fth | fluoranthene |
| Indo | indeno(1,2,3-cd)pyrene |
| Nap | naphthalene |
| Per | perylene |
| Phe | phenanthrene |
| Py | pyrene |

| | |
|---|---|
| DCM | dichloromethane |
| HCl | hydrochloric acid |
| ISO | isohexane |

### Samples and sample locations

| | | |
|---|---|---|
| GH | Gemeinde Heroldstatt (community of Heroldstatt), identifies the passive samplers | |
| SL | Stadt Laichingen (town of Laichingen), identifies the passive samplers | |
| BS | Bergstraße | = settlement |
| SoS | Sontheimer Schacht | = open territory |
| HWS | Hawaii-Schacht | |
| SH | Sontheimer Höhle | = forest |
| LTH | Laichinger Tiefenhöhle | |
| StH | Steingau-Höhle | |
| TK | Sächsische Schweiz (Laichinger Tiefenhöhle) | |
| VH | Vesperhalle (Laichinger Tiefenhöhle) | |
| NS | Nasser Schacht (Laichinger Tiefenhöhle) | |
| BT | Blautopf Spring | |

# CHAPTER 1

# INTRODUCTION

## 1.1 Motivation

With the beginning of the Industrial Revolution the release of pollutants increased strongly and caused different environmental problems. Through atmospheric transport they can reach locations far away from any industry, for instance the Arctic (MASCLET, 2000). From the atmosphere they can be deposited by dry (direct impact of particles and gaseous phase) and wet (all kind of precipitation) deposition. They accumulate in soils and sediments, from where they can enter the food chain and thus cause risk to the health of all creatures. Otherwise, they can be directly inhaled via particulate matter. The investigated pollutants, the polycyclic aromatic hydrocarbons (PAHs) are carcinogenic, mutagenic, and teratogenic. Another great problem is the risk to groundwater quality. Groundwater is frequently used as drinking water and, if the sorption capacity for contaminants of the soils is exhausted, they may break through and reach the groundwater.

A lot of laboratory and field work has been done to investigate the risk potentials from the different sources of PAHs. However, it is difficult to scale lab results up to the field. For this reason, this work was originated to study this problem directly in the field supported by lab experiments. GOCHT (2005) has already done a mass balance for PAHs in forest catchments. His finding was that almost all PAHs were accumulated in the soils. Due to this the most important question for this study was: Is this also valid for a karst area? Or do any transport processes take place? Can PAHs be used as reactive tracers in a karst area? Do conduits, fast flow, sinkholes, particles, etc. affect PAHs transport and if in which manner?

A karst system was chosen because of its higher vulnerability considering transport of contaminants. The infiltrating water can enter the karst system partially unimpeded along sinkholes and shafts. There it can reach the groundwater very fast due to fissures and conduits which assure fast transport. The chosen Blautopf Catchment is near Tübingen, so samples can be taken on a regular basis and the further processing in the lab can be rapidly done. Furthermore, the Blautopf Catchment was and still is a popular and well known research area. An advantage of this area is the possibility to enter the vadose zone in a karst area by caves to sample the seepage water which is normally (in a non-karst area) not possible and the availability of hydrology information.

In the study area (Blautopf Catchment) VILLINGER & UFRECHT (1989) measured flow velocities in the karst aquifer up to 350 m $h^{-1}$. Contaminants can be transported from the source to the outlet very fast, if they have once entered the fast conduit system (dissolved or particle associated).

Twenty-five % of the world's population uses karst water as drinking water (FORD & WILLIAM, 1989). This shows the importance of groundwater from karst systems for the water supply.

The largest part of the plateau of the "Schwäbische Alb" pertains to the “open zone” which is very permeable for precipitation. Only in the thin soil cover and the epikarst (subcutaneous zone) as well as in the rock matrix, retardation processes can take place (sorption, degradation, etc.). Because of this thin cover the karst water is very vulnerable to anthropogenic input of contaminants as nitrate, sulphate, chloride and pesticides.

## 1.2 Research Objectives

The aim of this project was to identify and qualify processes which are relevant for transport of PAHs at the catchment scale. This was reached by determining a mass balance which considered atmospheric deposition, accumulation in soils, the transport in the seepage and groundwater, and finally output at the outlet of the catchment, the Blautopf Spring. All sampling locations which have been involved can be seen in Fig. 1.1, a schematic overview of the karst area.

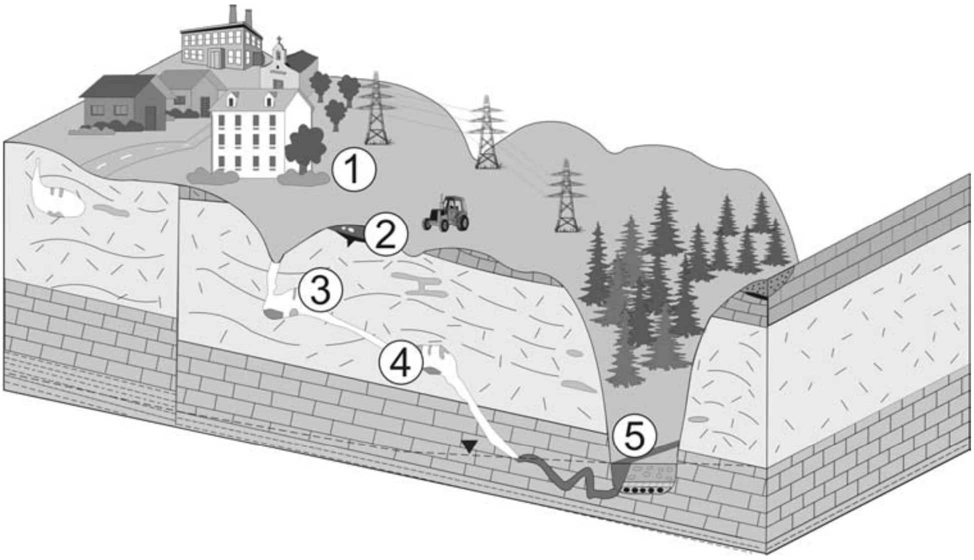

**FIGURE 1.1:** Sampling locations for determining the mass balance: ① INPUT: atmospheric deposition, ② soil accumulation, ③ seepage water (cave), ④ cave sediments and ⑤ OUTPUT: groundwater (spring). Graph changed according to VILLINGER, 1986.

First the atmospheric deposition was determined to get the input rate of PAHs into the system. Therefore, a passive sampler device was used, which could collect both the wet and the dry deposition. The next step was to analyse the different soil horizons. PAHs are hydrophobic and prefer to adsorb into the organic matter, which means that the top soil is the main accumulator. If the PAHs get displaced, they will appear in the seepage water before they reach the groundwater. The best way to analyse the seepage water in a karst area is to go into the caves and directly collect the infiltrating water. For analysing the seepage water, the same passive sampler device as before, but in a modified form, was used. To get information from former displacements, the cave sediments were also checked for PAHs. Finally, the output of the system was monitored. This was done at the karst spring, the Blautopf, with a specially designed sampling device. Output fluxes of PAHs were measured using peristaltic pumps which sample the water in the spring continuously with average flow rates of 10 ml min$^{-1}$. With all this data, it was possible to establish an input/output mass balance of PAHs to assess the risk of groundwater quality in the investigated area. A detailed presentation of the different investigation steps is given in the Fig. 1.2.

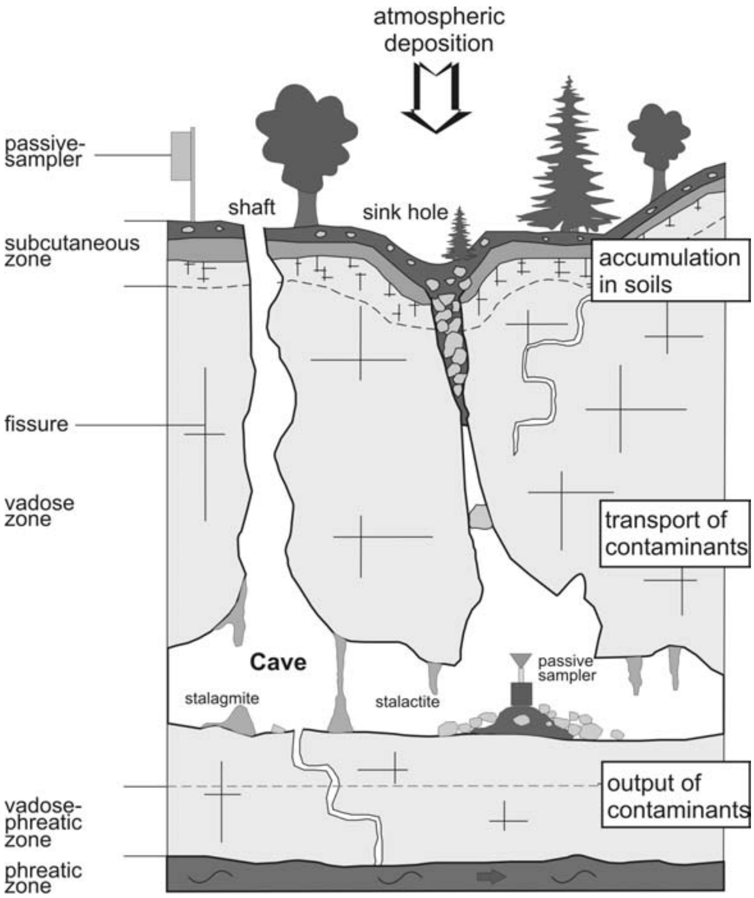

**FIGURE 1.2:** The conceptual model of contaminant storage and transport (atmosphere, soil, seepage and groundwater).

**The main objectives of this study were:**

- Development of a method for quantification of fate and transport of organic pollutants at the field scale (from atmosphere to soil, seepage water, cave sediments and spring).
- To establish input/output mass balances at the catchment scale, to make some statements about the risk to groundwater quality in this karst area.
- To determine the main transport process of pollutants in the karst aquifer (dissolved or associated with particles).

## 1.3 Format of the Thesis

The thesis is subdivided into different chapters which present the investigated compartments. Each chapter contains the following headers:

- Introduction, which shows the actual state of the art
- Sampling Sites, which gives an overview about the different locations and their aspects
- Material and Methods, in which the used methodology is described
- Results and Discussion, here the results are presented
- Summary

In Chapter 2 a general overview of the area of investigation is presented. The following chapters deal with the atmospheric deposition of PAHs (3), their accumulation in soils (4) and the desorption of PAHs from soils into seepage water (5). In chapter 6 and 7 the transport in the seepage and groundwater is presented. Chapter 8 summarises the data from the former chapters to provide a comprehensive mass balance considering all compartments. In chapter 9 the results from the isotopic investigations are given, which supplements the data on PAHs in the former chapters.

Each chapter of this thesis was written more or less independent of the others, so it can be read without knowing the others. Every chapter contains the fundamentals to understand the findings of this work. All used abbreviations can be found at the beginning of the thesis.

## 1.4 Study Significance

This monitoring program was organised to determine the spatial and temporal impact of anthropogenic influence in a rural karst area. It was possible to get information about the sources of PAHs, the transport processes, and thus the risk for groundwater quality in this karst area. The combination of different research topics (pollutants, hydrogeology and isotopes) facilitated the understanding of flow and transport in karst areas.

## 1.5 References

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# CHAPTER 2

# SAMPLING LOCATIONS

## 2.1 Selection of the Catchment

A karst area was chosen because of its high vulnerability and the potential for breakthrough of PAHs during heavy rain events or snowmelts. The “Schwäbische Alb” (Southern Germany) forms together with the “Fränkische Alb” the largest karst area in Germany. This is a mountain range which is part of the German escarpment landscape. It stretches from southwest to northeast at a length of around 200 km and a width of ca. 40 km. The study area is located on the plateau of the “Schwäbische Alb”, draining all the water to the karst spring – the Blautopf. The Blautopf is the second largest karst spring in Germany. The catchment has a size of 165 km$^2$ and is presented in Fig. 2.1, where all sampling locations are shown. It is a rural area with little industry. There are more than 50 caves situated in the catchment. For this investigation four of them have been chosen, two of them are show caves:

- "Laichinger Tiefenhöhle" (LTH)
- "Sontheimer Höhle" (SH)
- "Hawaii-Schacht" (HWS)
- "Steingau-Höhle" (StH)

They have different locations in terms of settlement and landscape. Furthermore, sampling locations in the caves, which are described later on, are placed in different depths beneath the surface. With this approach we tried to follow the contaminant transport paths in the system. The groundwater reaches peak velocities up to 350 m h$^{-1}$. This means that the seepage water which entered the aquifer can reach the spring in only 2-3 days. The west border of the catchment is established by the European water divide between the river Rhine and the Danube systems.

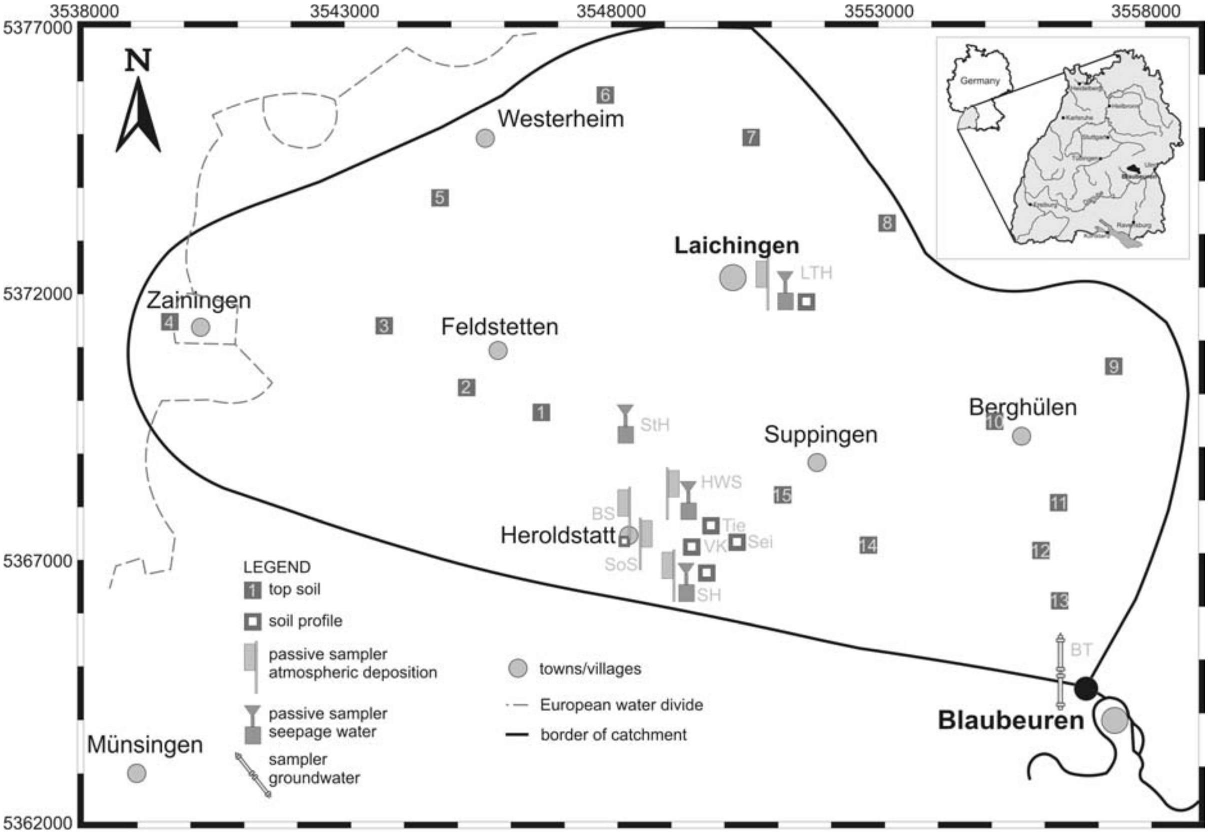

**FIGURE 2.1:** The catchment area with all sampling sites. Numbers indicate soil samples to be found in the appendix.

**TABLE 2.1:** Latitudes and longitudes of the sample locations.

| sample location | latitude | longitude | estimated depth below ground [m] |
|---|---|---|---|
| precipitation station | 48°26’39’’ N | 9°40’01’’ E | - |
| *atmospheric deposition:* | | | |
| GH BS | 48°26’39’’ N | 9°40’01’’ E | - |
| GH HWS | 48°27’29’’ N | 9°40’52’’ E | - |
| GH SH | 48°25’52’’ N | 9°41’02’’ E | - |
| GH SoS | 48°26’21’’ N | 9°40’22’’ E | - |
| SL LTH I + II | 48°28’43’’ N | 9°41’36’’ E | - |
| *caves:* | | | |
| LTH | 48°28’43’’ N | 9°41’36’’ E | -33 |
| HWS | 48°27’29’’ N | 9°40’52’’ E | -8 |
| SH | 48°25’52’’ N | 9°41’02’’ E | -45 |
| StH | - | - | -6 |

# CHAPTER 3

# SEASONAL BULK ATMOSPHERIC DEPOSITION OF PAHS IN A RURAL CATCHMENT IN SOUTHWESTERN GERMANY

## Abstract

Polycyclic aromatic hydrocarbons (PAHs) were measured in the bulk atmospheric deposition of a rural area in southern Germany for a two-year period using a passive sampler device. The bulk fluxes of PAHs ranged from 56 to 1983 ng $d^{-1}$ $m^{-2}$, the highest fluxes were measured in a settlement. Atmospheric deposition was dominated by high molecular weight PAHs indicating prevalence of particulate phase deposition. All locations showed the same distribution pattern and similar concentrations, which indicated that the input is very constant over a large distance. The passive samplers are reliable to determine the atmospheric deposition. During winter the bulk deposition was highest indicating household heating as main input source. Leaves have also been sampled in the same area. They can be considered as biological passive samplers. The concentrations in the leaves, sampled in autumn, varied between 82 and 675 ng $g^{-1}$ (dry weight). In opposite to the passive sampler device they accumulate the lighter PAHs from the gaseous phase.

**Keywords:** PAHs, monitoring, passive sampler, bulk deposition, leaves, atmosphere, biomarker

## 3.1 Introduction

Emission of PAHs into the atmosphere from combustion-related emission sources led and still leads to a ubiquitous contamination of the environment. PAHs are generally formed by incomplete combustion of fuels. The greatest share of PAHs is released by human activities such as burning of fossil fuels, coal gasification, or oil refining (HOWSAM and JONES, 1998). The transport behaviour of these PAHs, which belong to the semi-volatile organic compounds (SVOCs), depends on their physiochemical properties, such as vapour pressure, and on the temperature. Because of the wide vapour pressure range covered, airborne PAHs can exist in both gaseous and particulate phase. The latter is often in association with small carbon particles (black carbon), which act as the most important carriers (DACHS and EISENREICH, 2000). Particularly, the less volatile 5-6 ring PAHs are bound to particles and the volatile 2 and 3 ring compounds exist in both the gaseous and particulate phase of the atmosphere (HOWSAM et al., 2000). Most PAHs are mutagenic, carcinogenic, and teratogenic. 16 PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (EPA, 1993). They have also been listed in the European list of priority pollutants (DIRECTIVE WATER FRAMEWORK, 2000).

Long-range transport is the main distribution factor of PAHs in the atmosphere. According to HOWSAM et al. (2001a), in rural locations the deposition of PAHs occurs as a result of emission and transport from a variety of diffuse, intermittent sources which are at some distance. PAHs are removed from the atmosphere by wet (precipitation, scavenging) and dry deposition (gas absorption, gravitational setting, eddy diffusion), which limits their travel distance from their sources. In addition, during long-range transport, PAHs undergo a number of processes such as degradation, deposition onto soils, vegetation or water bodies, sedimentation and bioaccumulation (FERNÁNDEZ and GRIMALT, 2003). Precipitation events facilitate the downward transport of persistent organic pollutants (POPs) (MATZNER, 1984).

Usually, PAHs in air are sampled with glass-fibre filters (MOTELAY-MASSEI ET AL., 2006), polyurethane foam plugs (HUNG et al., 2005; MOTELAY-MASSEI et al., 2005), XAD resin (MORVILLE et al., 2004; WANIA et al., 2003) or quartz filters (HE et al., 2006; SHIMMO et al., 2004). Passive samplers are preferably used because they do not require any electricity or any other power source to operate (BARTKOW et al., 2005). For this work a passive sampler device was employed to allow for time integrated long-term monitoring.

Over the last decade the use of plants as biological passive sampler has been developed (ERIKSSON et al., 1989; HOWSAM et al., 2000; LODOVICI et al., 1994; MÜLLER et al., 2001; PICCARDO et al., 2005) because vegetation can scavenge contaminants from the gaseous and particulate phase of the atmosphere (BARTKOW et al., 2004; MCLACHLAN, 1999). This uptake of PAHs from the atmosphere allows for use of the vegetation as bioindicator. Generally, it is accepted that the bulk of the PAHs burden associated with vegetation, especially trees, is derived from the atmosphere, rather than from soil (SMITH and JONES, 2000). However, all vegetation which is below 0.5 m height can be contaminated by soil (SMITH and JONES, 2000). It is necessary to have a profound understanding about sorption processes on vegetation surfaces, since according to MCLACHLAN (1997) this is the first step in the food chain, which finally can affect all subsequent food chain members.

The objective of this study was to measure absolute rates of the atmospheric bulk deposition over a two year period and to identify input sources, as well as the different transport and deposition processes. Various locations were chosen to get information about the influence of diverse boundary conditions, such as open territory, forest, and settlement. The input of PAHs was used for an input/output mass balance in a karst area to evaluate the risk of groundwater pollution and the main processes which are important for the fate and transport of contaminants.

This research was part of a groundwater risk assessment study in a karst system using ubiquitous organic contaminants as tracers. The idea was to determine a mass balance which considered atmospheric deposition, accumulation in soils, the output in the seepage and groundwater. The atmospheric deposition represents the input of PAHs. In principle is the Blautopf Spring the only outlet of the catchment system, a small, but negligible spring is located nearby ("Gerhauser Quelle"). This means that all rainwater that infiltrates into the underground will sooner or later be captured in the Blautopf. With the concentrations of PAHs in the spring, the output can be calculated and the mass balance established.

## 3.2 Materials and Methods

### 3.2.1 Sampling Sites

The Blautopf Catchment is located on the plateau of the “Schwäbische Alb”, southern Germany (Fig. 2.1). The altitudes vary between 512 m at the Blautopf Spring and 900 m at the west end, with a slope from west to east. The area has low population density (130 people/km$^2$) with relatively little industry. The biggest town in the catchment is "Laichingen" with around 11000 inhabitants. The "Schwäbische Alb" is located in the continental climate zone, the precipitation varies from 800 to 1100 mm $a^{-1}$ (KELLER, 2003). More catchment characteristics are compiled in Table 3.1.

**TABLE 3.1:** Characteristics of the catchment.

| | Comments |
|---|---|
| Catchment area | 165 $km^2$ |
| Land use [a)] | settlement: 7.9 %<br>forest: 30.9 %<br>open territory: 61.2 % |
| Average rainfall [b)] | 1057 mm $a^{-1}$ |
| Average temperature [b)] | 7.0 °C |
| Population equivalent | ~130 people $km^{-2}$ |
| Average outflow (Blautopf) [c)] | 2.43 $m^3$ $s^{-1}$ |

a) changed according to KÖBERLE (2005)
b) (POSTIGO REBELLO, 2006)
c) 1980-2003 (http://www.hvz.baden-wuerttemberg.de/)

The study was carried out between June 2004 and July 2006. Thus two complete years were covered for monitoring. The passive samplers were located in five different locations near "Heroldstatt" and "Laichingen" in the Blautopf Catchment:

- GH SH: 9°41’02’’ E & 48°25’52’’ N, located in a beech forest
- GH BS: 9°40’01’’ E & 48°26’39’’ N, located in the village "Heroldstatt"
- GH SoS: 9°40’22’’ E & 48°26’21’’ N, located on a grassland
- GH HWS: 9°40’52’’ E & 48°27’29’’ N, located in a valley near a small settlement
- SL LTH I +II: 9°41’36’’ E & 48°28’43’’ N, located above the cave of "Laichingen"

### 3.2.2 Passive Sampler Design

The main part of the sampling apparatus was arranged in a cylindrical box made of stainless steel, containing a glass funnel with a diameter of 25 cm (Fig 3.1). Connected to this funnel was a glass cartridge filled with 15 g of the adsorber material Amberlite™ IRA-743. The cartridge was fixed at a height of 1.2 m and the top of the glass funnel 1.6 m above. It is possible to collect wet and dry deposition with this system. For more details see GOCHT (2005), GOCHT et al. (2007a), MARTIN & GRATHWOHL (2002) and MARTIN (2000).

Leaves collected in the sampler were analysed separately. In July 2005 separate adsorption cartridges were installed to monitor for gas phase compounds. These cartridges were fixed to the top of the sampler at a height of 1.8 m and were covered by a lid, with a distance of 1 cm to the cartridge to allow gas diffusion, but to keep precipitation off (Fig. 3.1).

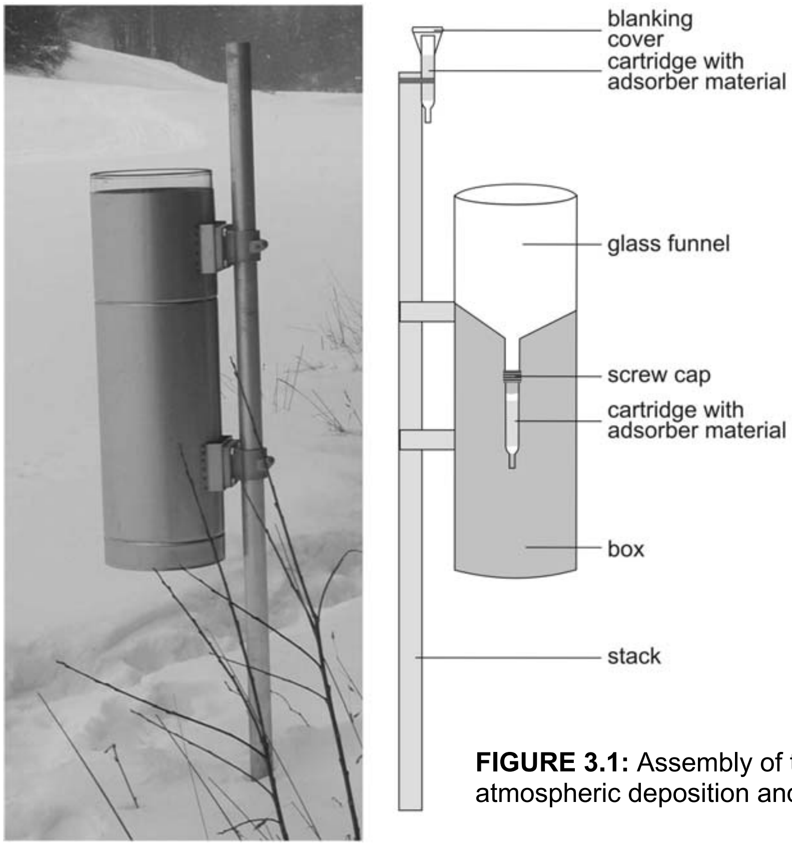

**FIGURE 3.1:** Assembly of the passive sampler device for atmospheric deposition and the gas phase sampler.

In general, the cartridges were exposed for two months. Initially longer campaigns had to be employed in some cases because of problems with impurities of the adsorber material. GOCHT (2005) and MARTIN (2000) showed that no breakthrough occurred over a period of three and six months, respectively. However, they determined smaller concentrations of the ∑PAHs contrary to cartridges with shorter exposition times.

After two months in the field the cartridge was removed and closed airtight for the transport to the lab. The funnel was cleaned with acetone-wet glass wool and consecutively rinsed with 200 ml acetone to assure that all PAHs from the glass funnel are collected.

Within 48 h the adsorber material, the glass wool, and the rinsing solution from the field were extracted. The glass wool was first placed into a 100 mL Luer Lock syringe with a stainless steel valve followed by the adsorber material. Afterwards the extraction was carried out in four sequential steps with 50 mL acetone each. The acetone, which was the rinse solution from the field, was kept two minutes in the syringe and subsequently it was gravimetrically released and totally emptied by the use of a plug. Next the surrogate standard was spiked to the total extract. 10 mL cyclohexane and 2 L Millipore water were added into the deuterated extract. Afterwards, the sample was shaken for one hour and kept for one day in the dark at ambient temperature. Finally, the cyclohexane which forms a separate phase was withdrawn with a syringe and concentrated to ~150 µL under nitrogen. In some cases, if separation of water and cyclohexane was not complete, the extract had to be treated with sodium sulfate ($Na_2SO_4$).

Subsequent to the extraction, the cyclohexane contained a lot of co-extracted compounds. Dark coloured extracts were purified with a cleanup on an alumina-silicic column (1:1) using different isohexane (ISO)-dichloromethane (DCM) mixtures to elute the sample (1. 30 mL pure ISO, 2. 5 mL 9:1 (ISO:DCM) and 3. 20 mL 4:1). Then the mixture was concentrated on a rotary evaporator to about 150 µL.

PAHs were analyzed on a Hewlett-Packard 6890 gas chromatograph equipped with a mass selective detector (HP-5973) using a DB-5 capillary-column (30 m x 0.25 mm). Surrogate standards (20 mg $L^{-1}$) consisting of five deuterated PAHs surrogates (naphthalene-d8, Ace-d10, Phe-d10, Chr-d12 and Per-d12) were added to the sample extract and used for the PAHs quantification. A diluted standard containing the 16 PAHs and the 5 deuterated surrogates was measured to calculate the relative response factors. To quantify the recovery an internal standard (Fth d-10) was added before the GC-MS measurement. This procedure gives information about the recovery of the surrogate standard and thus a loss of PAHs during the analyzing steps can be recognized.

For each sampling period a field blank was carried along and treated like a sample to check for cross contaminations during transport or handling in the laboratory. The samples and the corresponding blanks were analyzed together. The blank values are included in the appendix A along with the results.

During winter season (September - April) all cartridges were wrapped with adhesive foil and additionally put into an isolation box made of polystyrene. This was necessary because during thaw-freeze events on cold nights (temperatures as low as -28 °C), ice plugs in the cartridges sometimes caused cracks in the glass. The adhesive foil in such cases prevented total loss of the sample, because it kept the broken pieces together. Above -10 °C the isolation-box was efficient to protect the glass cartridge for breaking.

### 3.2.3 Leaf Sampling

Leaf sampling near "Heroldstatt-Sontheim" was conducted during two campaigns, one at the beginning of the vegetation growth phase 2005 in June (three samples) and the other in October at the end of autumn (nine samples). The spring leaves were directly picked from the tree by hand at a height of 1.5-2.0 m, whereas the autumn leaves were collected from the ground. Needles from conifers were only collected at the end of the branches (max. 10 cm), which have an estimated age of approximately one year. All leaves were placed in plastic bags only for transport, then they were dried at ambient temperature till a constant dry weight was achieved.

The leaves were analysed with the accelerated solvent extraction device (ASE). The equipment and method is described in detail in chapter 4. Samples of 4–11 g (dry weight) without leaf stalks were used for the analysis of PAHs. The samples were put into 33 mL extraction cells and placed between two layers of silica and glass-fibre filters at the ends of the cell. The extraction itself was done in two acetone (100 °C, 100 bar) and two toluene (150 °C, 100 bar) steps. Further processing of the extracts included addition of a surrogate standard. The acetone extract was dealt in the same way as the extract from the passive sampler cartridges (Chap. 3.2.2). The toluene extract was directly minimized to 150 µL with a rotation evaporator and if necessary with the nitrogen stream. Because of the co-extraction of natural organic compounds it was necessary to clean up all the leave extracts with the above mentioned column-chromatography-separation (Chap. 3.2.2).

### 3.2.4 Quality Control and Assurance

Special care was taken to assure that the adsorber material for the passive sampler device was free of background contamination and degradation. For this reason, the IRA was cleaned and tested in the laboratory before field use. This was done because the contamination on the adsorber could falsify the results and furthermore cause problems in the GC-MS analysis.

All material which was needed for sampling and analysis for this study was stored and analysed under special purity conditions. The used solvents and standards were tested for background contamination on a regular basis.

Recoveries for all atmospheric samples ranged from 11 % to 100 %, whereas the low values could be related to samples with co-extracted compounds with a complex clean-up, causing losses. The average recovery from GH SoS is given by Ace-d10 (50 %), Phe-d10 (54 %), Chr-d10 (57 %) and Per-d12 (62 %). The recovery increased with increasing molecular weight due to the PAHs transfer from the acetone-water mixture into the cyclohexane.

For the leaf analysis with the ASE several blank tests were conducted to exclude background contamination. Concentrations of all measured blanks were lower than the concentrations of the samples.

## 3.3 Results and Discussion

### 3.3.1 Deposition Rates

The bulk atmospheric deposition rates (gaseous and particulate) were in the range from 56-1983 ng $d^{-1}$ $m^{-2}$ [blank: 2-4 ng $d^{-1}$ $m^{-2}$] whereas the one in the village (GH BS) showed the highest and the one in the forest (GH SH) the lowest value. The yearly weighted mean averages were calculated with the following equation:

$$\chi = \sum_{i=1}^{n} \frac{D_i \cdot t_i}{365} \; [\mathrm{M\ L^{-2}\ t^{-1}}] \qquad [3.1]$$

where $\chi$ is the mean annual deposition rate, $D_i$ the deposition rate [M $L^{-2}$ $t^{-1}$] and $t_i$ the duration of the sampling period [t]. The weighted mean average for the five sampling locations in the first/second year was 590/484 ng $d^{-1}$ $m^{-2}$ (GH BS), 187/177 ng $d^{-1}$ $m^{-2}$ (GH SH), 254/195 ng $d^{-1}$ $m^{-2}$ (GH SoS) and 215/152 ng $d^{-1}$ $m^{-2}$ (GH HWS) [blank: 23/13 ng $d^{-1}$ $m^{-2}$]. The deposition rates for the two year sampling period are displayed in Fig. 3.2.
The values for the location SL LTH are given as a two year average: 288 and 221 ng $d^{-1}$ $m^{-2}$ (I + II) [blank: 12 ng $d^{-1}$ $m^{-2}$]. The sum of the six carcinogenic PAHs, like BaA, BbF, BkF, BaP, DahA, and Indo (ENVIRONMENTAL HEALTH INFORMATION SERVCIE (EHIS), 2005) showed values of 14/4 and 328/260 ng $d^{-1}$ $m^{-2}$ [blank: 0–1/2 g $d^{-1}$ $m^{-2}$] in the first/second year for the GH samplers. The percentage of these carcinogenic PAHs was significant i.e. 25/8-30/38 % [0-22/21 %] of the ∑PAHs.

The distribution patterns of PAHs show that on average Phe was the dominating substance (23 %) followed by Fth (17 %), Py (11 %), BbF (8 %) and Chr (7 %). BbF, one of the carcinogenic PAHs, is the fourth most commonly deposited. There was no significant difference in the pattern between the various locations and seasons (Fig. 3.2). All locations showed seasonal fluctuations in their concentrations with 2-4 times higher deposition rates during winter as already observed by others (BRUN et al., 2004; GOCHT et al., 2007a; HALSALL et al., 1997; MOTELAY-MASSEI et al., 2003). The highest deposition rate was found in the village. This shows directly the effect of domestic space heating during the cold season (BRUN et al., 2004); this seasonal signal was only local and did not reach sampling location GH SoS, which was around 1 km south. Since the prevailing wind direction in southern Germany is west, most of the locally produced PAHs are presumably transported in eastern direction. The next biggest city westward of the catchment is "Bad Urach" which is about 10 km from the western borderline away and 400 m lower of altitude. Because of the “Albtrauf” a lot of wind and rain gets stopped at the ascent and does not reach the study area.

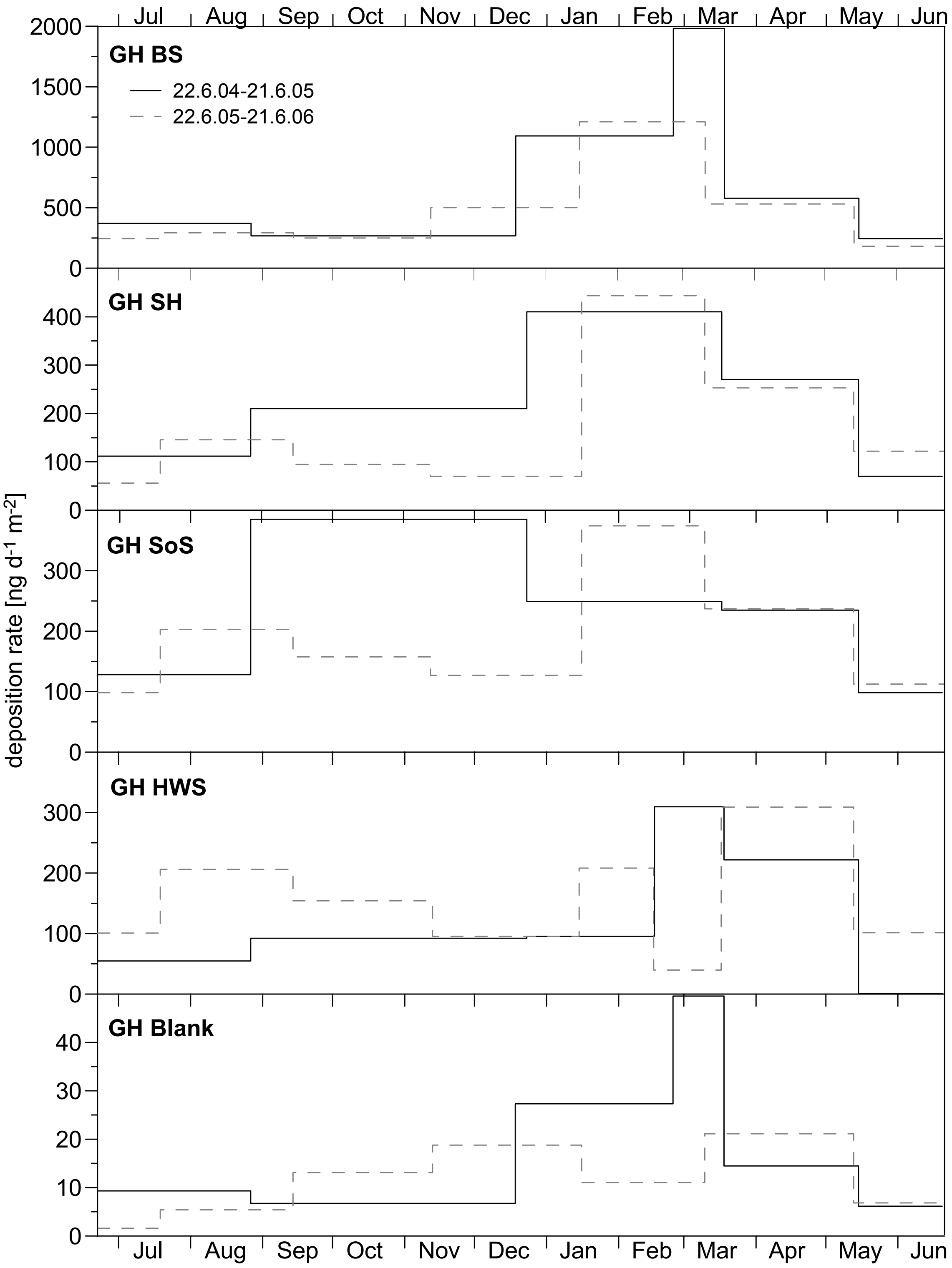

**FIGURE 3.2:** Bulk atmospheric deposition rates for ∑PAHs [ng $d^{-1}$ $m^{-2}$] at different locations for 04/05 and 05/06. Note the different scales. The abbreviations denote locations: BS = village, SH = beech forest, SoS = open territory and HWS = valley.

The two samplers from SL LTH showed also seasonal changes (appendix A). The seasonal cycle was more pronounced in the second year. The deposition rates of both samplers were very similar; there were only slight variances and one outlier at the end of the sampling period. This shows that the two samplers, which have been positioned 20 m from each other, accumulated the same input and thus the atmospheric deposition is homogenous. All mean annual deposition rates range from 177-288 ng $d^{-1}$ $m^{-2}$ (without settlement), this means that the input was very stable during the 2 years monitored. Furthermore, the deposition rates and the distribution patterns are spatially very constant considering the atmospheric deposition over a large area.

Here, low molecular weight PAHs (LWM-PAHs) are defined from 128-178 g $mol^{-1}$, namely Any, Ace, Fln, Ant and Phe. Accordingly, high molecular weight PAHs (HMW-PAHs) are BbF, BkF, BaP, BeP, Per, Indo, BghiP and DahA and range from 252-278 g $mol^{-1}$. In between, there are the intermediate PAHs (Fth, Py, BaA, Chr).

The ratio of HMW-PAHs to LMW-PAHs varied between 0.1 and 3.0. The ratio in summer time typically lies > 1 and in winter it is around or below 1. This result reflects the effect of cold condensation, which means that the LMW-PAHs undergo dry deposition during winter (BLAIS et al., 1998; CARRERA et al., 2001; WANIA et al., 1998). Rainfall scavenges the particle associated species to a greater extent than the vapour phase compounds (PREVEDOUROS et al., 2004). MOTELAY-MASSEI et al. (2005) reported that HMW-PAHs which are associated with particles will be deposited closer to the source. Thus there is a fractionation along (long-range) transport in the atmosphere which varies during the different seasons.

It was difficult to associate the different seasons with varied sources of PAHs. For example, the ratio BghiP:BeP is thought to be indicative of vehicle exhaust (NIELSEN, 1996). The ratios here reach a maximum of 2.5, whereas the average was 1.2. These values give evidence that PAHs deposition does not correlate with traffic sources. Only the values which are higher than 1.4 can be attributed to traffic sources.

Campaigns which sampled PAHs only in the gaseous phase of the atmospheric deposition reported higher rates in summer, because of volatilisation from surfaces like soils, roads, vegetation, or water (LI et al., 2006; MOTELAY-MASSEI et al., 2005). For particulate analysis the opposite relation exists, low rates of PAHs in summer and high ones during winter (GUO et al., 2003; WILD and JONES, 1995). The passive sampler device employed in this work accumulates prevalently the particulate phase. Obviously, the amount of gas phase deposition rates of the compounds is relatively low.

The ratio BeP:BaP gives information about the source and transport of PAHs (LI et al., 2006), because BaP is easily decomposed by light and oxidants (GRIMMER et al., 1983). The normal ratio in this study ranged among 0.9 to 1.5, which indicates that degradation of BaP is relatively low and the PAHs associated with the particles are fairly stable or sources are fairly close.

### 3.3.2 The Use of Plants as Passive Samplers (PAHs Concentrations in Leaves)

The ∑PAHs of deciduous trees collected in October were between 424 ng $g^{-1}$ and 675 ng $g^{-1}$ (dry weight), the ones of the conifers were lower and were 82 and 249 ng $g^{-1}$. All results are given in Table 3.2.

The mean distribution pattern of PAHs of deciduous trees resembles the one from the gas deposition samplers: Phe (55 %), Fth (16 %), Py (12 %), Fln (6 %) and Chr (2 %). These five compounds represent 91 % of the total ∑PAHs. This indicates that the uptake of PAHs in leaves is dominated by the gaseous phase. PICCARDO et al. (2005) also found LMW-PAHs dominating in pine needles. They explained this by a more rapid diffusion and accumulation of volatile PAHs into the inner compartment. This fits with the finding from NIU et al. (2003), who stated that photolysis plays an important role on the fate of PAHs sorbed on the surface of spruce needles. In a lab experiment they found that photolysis half-lives range from 15 h for DahA to 75 h for Phe and thus PAHs in the inner compartment are more stable.

**TABLE 3.2:** Concentrations of different leaves in spring and autumn [ng $g^{-1}$].

| **Tree species** | **Concentration [ng $g^{-1}$]** | |
|---|---|---|
| | October 2005 | June 2005 |
| apple tree | 559 | - |
| aspen | 675 | - |
| basswood | 611 | - |
| beech | 663 | - |
| chestnut | 464 | - |
| fir | 82 | 17 |
| maple | 424 | n.d. |
| oak | 559 | - |
| pine | 249 | n.d. |

Another possibility is the higher concentrations of LMW-PAHs in the gaseous phase. PAHs sorbed to the surface of leaves or needles are more easily exposed to external environmental factors (e.g. rain, heat, ozone, solar radiation). A good method to estimate the partition between air and plant is the octanol-air partition coefficient $K_{oa}$ (BACCI et al., 1990). According to KRAUSS et al. (2005) plants take up organic compounds up to log $K_{oa} < 8.5$ by equilibrium partitioning with the gas phase, for $8.5 < \log K_{oa} < 11$ by kinetically limited gaseous deposition and for log $K_{oa} > 11$ by particle bound deposition. HOWSAM et al. (2000) recognized that concentrations of the larger, more lipophilic PAHs were generally higher than the smaller, more volatile compounds. They concluded that hairy leaves are more effective at retaining impacted particles on their surfaces. Note that the leaves analysed in this study did not belong to hairy species.

HMW-PAHs were only detected in conifers, even though in small amounts. The five most common PAHs in the fir sample were Phe (38 %), Fth (16 %), Py (13 %), Ace (6 %) and Chr (5 %). The HMW-PAHs accounted for 12 % in the fir and only for 2 % (mean average) in the deciduous leaves (Fig. 3.3). This indicates that different plants accumulate different PAHs because of physical and chemical properties of the pollutants and leaf lipid content and the specific available surface.

SMITH & JONES (2000) and UMLAUF & MCLACHLAN (1994) reported a dependence of particle bound SVOCs to vegetation on the particle deposition velocity, the substance concentration on the particle, the residence time, and the transfer of the substance from the particle to the leaf during this period. Considering all these factors it is obvious that the HMW-PAHs show only low concentrations. Furthermore, a major uptake process of lipophilic organic contaminants is given by the gaseous diffusion from the air to the waxy layer in plant leaves (MCLACHLAN et al., 1995). This means the leaf uptake from air is limited by the air concentrations, consistent with the theory of air/plant partitioning (KÖMP and MCLACHLAN, 1997). MIGASZEWSKI et al. (2002) found out that the number of aromatic rings was inversely proportional to the appearance of each PAHs.

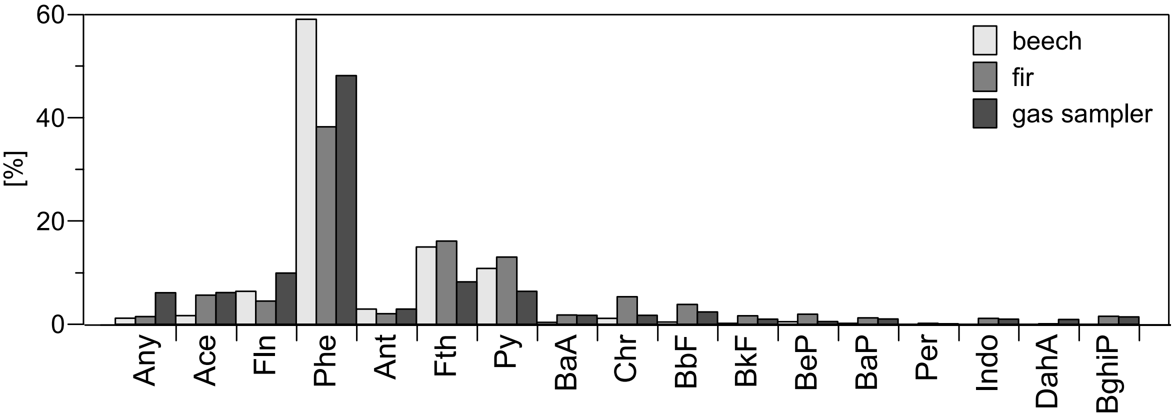

**FIGURE 3.3:** Comparison of PAHs distribution of a deciduous tree (beech) a conifer (fir) and a gas sampler (GH SH, mean average)

The concentrations of ∑PAHs of the analysed leaves are fairly high in comparison to other studies (e.g. HOWSAM et al., 2001b). This can be due to different extraction methods, e.g. sonication (PICCARDO et al., 2005), Soxhlet (HOWSAM et al., 2000; HOWSAM et al., 2001a; HOWSAM et al., 2001b) or extraction with dichloromethane (HWANG et al., 2003). Additionally, HUBERT et al. (2003) confirmed that the extraction efficiency was improved by up to two orders of magnitude by ASE compared to conventional methods. LODOVICI et al. (1994) found values between 72 and 588 ng $g^{-1}$ in autumn and 88 and 880 ng $g^{-1}$ in winter while considering nine PAHs in rural and urban areas near Florence, Italy. WILD et al. (2005) explain why PAHs are continuously present in leaves, although a permanent photodegradation exerts influence on the PAHs:

(a) they are constantly generated and supplied fresh from the atmosphere
(b) it may be dark/cloudy when they are supplied

(c) once they start to penetrate into the leaf, they become more protected from photo-degradation
(d) many leaves are "self-shaded" in the field.

HOWSAM et al. (2001a) report that litter layers during winter had higher burdens of PAHs than directly after litterfall. They referred this to a significant input in direct wet and dry deposition between December and February. Furthermore, they determined that the more volatile and water soluble PAHs were not accumulated to a large degree in the system, while the heavier ones accumulated in the soil. These conclusions coincide with the findings of this work. Evidence was found that the burdens of PAHs in leaves contribute to the accumulation in soils as indicated by distribution patterns in forest soils. The LMW-PAHs did not show a higher occurrence. On this account the concentration of the leaves are not used in the mass balance later on (Chap. 8).

In Fig. 3.4 a comparison of a leaf, the time integrated sampler in the forest, and a forest top soil (GH Sei) is presented. A depletion of Phe can be observed: leaf > integrated sampler > soil. This depletion can be caused by degradation and/or revolatilisation (GOCHT et al., 2007b). With increasing degradation of organic matter in woodland systems, HMW-PAHs become selectively enriched (GUGGENBERGER et al., 1996), since, as it is known, the degradation rates of PAHs decrease with molecular weight of the compound (BOSSERT and BARTHA, 1996).

In general the bulk atmospheric deposition in the catchment was lower in the forest than in the open field. This means that part of the PAHs input is retained by the canopy of leaves. However, there is no difference between the distribution pattern of the deposition of the open field and the one in the forest.

If the biomass of the leaves is known, than it should be possible to estimate the total deposition of PAHs via biomass. TRAPP (2001) established a biomass distribution in a Central European Quercus-Carpinus deciduous forest. There the leaf biomass was four tons per hectare. With the mean average of the nine autumn samples of the study area, the total ∑PAHs concentration of the leaf biomass would be about 11 kg. This result is as high as the determined deposition rates and shows that the biomass acts as an important sink for organic pollutants unless revolatilisation and biodegradation are not considered.

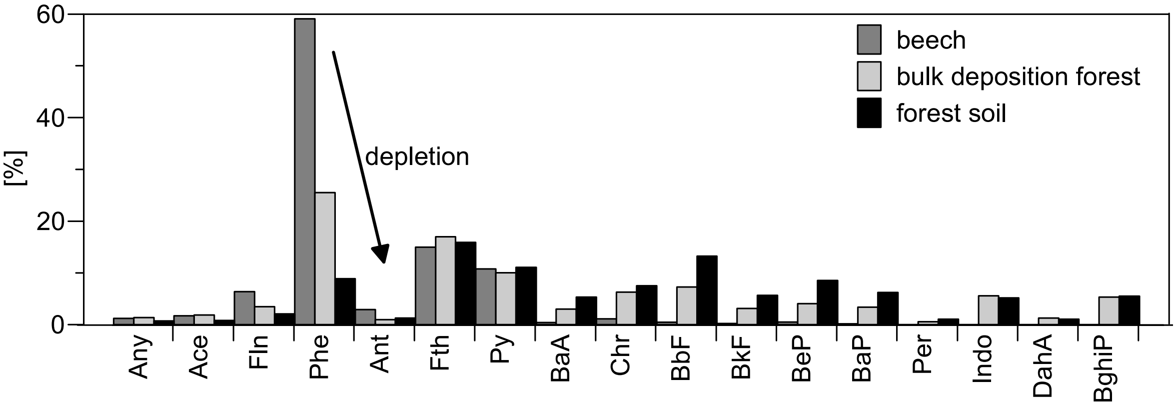

**FIGURE 3.4:** Depletion of Phe from a beech leaf to a forest soil.

## 3.4 Summary

The investigation of the atmospheric deposition in the rural area of the Blautopf Catchment with time-integrating deposition samplers showed following main results:

- The bulk atmospheric deposition rates into the Blautopf Catchment showed a seasonal cycle with higher values during winter. The mean annual deposition rates were very consistent for all locations, varying in the range of 187-254 ng $d^{-1}$ $m^{-2}$ (1st year) and 152-195 ng $d^{-1}$ $m^{-2}$ (2nd year) (without settlement).
- During winter the highest deposition rate was found in the village (1983 ng $d^{-1}$ $m^{-2}$). This result shows directly the effect of domestic space heating during the cold season.
- The distribution pattern of PAHs showed clearly that the bulk deposition is associated with particles.
- PAHs in leaf samples in autumn had concentrations in the range of 424-675 ng $g^{-1}$. These are rather high concentrations. The distribution patterns showed that the uptake of PAHs was from the gaseous phase.

In general, a combined determination with the passive sampler and the vegetation samples was a simple way to get information about the atmospheric input of PAHs. Preparation and analysis of the leaves give good results with less effort. The passive samplers proved to be reliable for the determination of the atmospheric deposition rates in the study area.

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# CHAPTER 4

# DISTRIBUTIONS AND CONCENTRATIONS OF PAHS IN SOILS OF THE BLAUTOPF CATCHMENT

**Abstract**

Samples from top soils and soil profiles were collected over an area of 165 $km^2$ to get information about the spatial distribution of PAHs at the regional scale. The total concentrations of PAHs showed values up to 20 mg $kg^{-1}$. Overall, the results show that soils accumulate PAHs. The depth distribution indicates the low mobility of the pollutants within the soil profiles. The highest PAHs concentrations were found in the top soils, which means they are the most important factor for fate of PAHs in a catchment. Atmospheric deposition was identified as the main input pathway by means of similar distribution patterns of PAHs in both media. Atmospheric deposition rates and concentrations in soils indicate that the German precaution limits could be exceeded in 64 years.

**Keywords:** Soils, Freundlich coefficient, inventories, PAHs, sorption isotherms

## 4.1 Introduction

Hydrophobic POPs are widely distributed through the global environment via long-range atmospheric transport and accumulation in soils and sediments. According to MEIJER et al. (2003) other sources of PAHs like sewage sludge disposal account only for a very small percentage considering the input into soils. Soils act as sinks for atmospherically derived PAHs because of their large sorption capacities for such compounds. Because of their high persistency, PAHs are amongst the compounds subject to international atmospheric emissions controls under the 1998 United Nations Economic Commission for Europe Protocol to reduce emissions (1998). PAHs can be found even in soils and sediments of remote areas far away from the initial source (FERNÁNDEZ et al., 2000).

A clear coherence between atmospheric deposition and soil burdens is given by GOCHT & GRATHWOHL (2004) due to analogue distribution patterns. The historical record of PAHs inputs into soils and sediments over the last 200 years is well known based on several sediment studies (MÜLLER et al., 1977; SANDERS et al., 1993; SIMCIK et al., 1996). With the beginning of the Industrial Revolution, an obvious increase of PAHs was documented. The peak level was attained in 1950-1975, since then the concentrations decreased as a result of a switch from coal to oil and natural gas, as well as air emission regulations (SIMCIK et al., 1996).

The uptake or release of PAHs depends on the distribution between the soil matrix and the solute phase. Sorption is quantified by the distribution coefficient $K_d$, defined as the amount of PAHs in the solid ($C_s$) to the concentration in the aqueous phase ($C_w$). Since many data on sorption of hydrophobic organic pollutants indicate nonlinearity of sorption, the $K_d$ values depend on contaminant concentrations to some extent (KLEINEIDAM et al., 2002; WANG, 2006).

Sorption of hydrophobic organic compounds (HOCs) in soils and sediments is mainly controlled by the organic matter (OM) contained in these materials (KLEINEIDAM et al., 1999). Additionally, the type of the OM is important. Generally normal soil organic matter sorbs less than thermally altered carbonaceous materials (black carbon, chars, coals). Sorption is a major process influencing the fate and transport of HOCs in soils (PAN et al., 2006). Nonlinear sorption isotherms can be attributed to a pore-filling mechanism, which is often superimposed by a partitioning-process. Sorption thus can be described by combined models, based on the Polanyi-Dubin-Manes's model (nonlinear) and the partitioning concept (linear).

As a result of changing temperatures, PAHs can be exchanged between soils and atmosphere. On a global scale this process leads to an increasing contamination of soils in colder regions (“global distillation”) (ABRAHAM, 2002).

Degradation efficiency of PAHs in soils is dependent on many different factors like temperature, pH-value, and bioavailability of microorganisms. Photodegradation is only possible in the uppermost part of the top soils, because of the short penetration depth of light. The low water solubility and strong sorption to organic material can limit the bioavailability for microbial degradation.

The objectives of this study were to identify the input sources of PAHs and the storage capacities of the different soil types. This was done with the help of source assessment by means of comparison of PAHs-fingerprints in atmospheric deposition and soils. Attention was also given to the total soil burden in the catchment. Furthermore, the role of soils in the overall fate of persistent organic pollutants was investigated, especially the function of soils as filters for hydrophobic organic pollutants. For the soil part, the main question was: Can the pollutants breakthrough or not? The highest sensitivity has to be expected in karst areas due to the thin soil cover and the direct pathways to the groundwater (e.g. sinkholes). Cave sediments were used to determine breakthroughs because they may accumulate PAHs as well. If the pollutants were efficiently retained by the soils, there should be no translocation with seepage water into deeper parts of the unsaturated zone. In this case some other questions need to be answered: Are the pollutants stable in the soils? Which is the main factor considering accumulation versus degradation?

## 4.2 Materials and Methods

### 4.2.1 Sampling Sites

The Blautopf Catchment is situated on the "Schwäbische Alb", which forms together with the "Fränkische Alb" the southeastern margin of the German cuesta landscape. Essentially the "Schwäbische Alb" is composed out of layered and massive limestones with some marlstones and dolomites of the Jurassic. The catchment itself has a size of around 165 km$^2$. The Blautopf Spring is the only outlet of the system with exception of a small spring nearby ("Gerhauser Quelle").

The soils are particularly developed in weathered limestone, which are very heterogeneous (GIEßL and HURLE, 1984). The main soil type in the Blautopf Catchment is a “Rendzina” (rendzic leptosol), others are “Braunerde” (cambisol) and “Kolluvisol” (redeposited soil of high thickness). The present soils evolved in the last 10000 years

(KÖBERLE and KÖBERLE, 2002). The surface of the Upper Jurassic limestone was influenced by the last ice age. Since the Tertiary, typical karst phenomena have been formed, like dry valleys, sink holes and caves. The ages of the investigated caves are estimated to be about 3-5 Ma old.

### 4.2.2 Soil Samples

Two different types of soil samples were taken during this investigation. The first ones were only top soils of agricultural land and the others were soil profiles of different land use (i.e. forest, grassland, etc.). The exact sample points can be seen in Fig. 2.1. All samples which are named EGBO are soils of agricultural land. The others are named like “BP SH I”, where BP is the description for the soil sample ("Bodenprobe"), SH the location ("Sontheimer Höhle") and the number indicates the identity if several samples were taken at the same location. Further information about the type of soils of this area can be found in KÖBERLE (2005). In total 40 samples were taken.

### 4.2.3 Cave Sediments

Samples were taken in two caves, the “Laichinger Tiefenhöhle” (LTH) and the “Sontheimer Höhle” (SH). A table with the sample locations can be found in Chap. 2. The sampling places in the caves were the “Sächsische Schweiz” (TK) in the LTH and “Wettergrenze” and “Wasserfall” in the SH. These places were around 33 m, 47 m and 33 m below the surface, respectively.

The cave sediments are red brown clays which have only a small part of coarser components and almost no organic matter. According to BURGER et al. (1993) the main part of cave sediments was produced by in-situ dissolution of the Jurassic limestone (autochthonous), but they also quoted an allochthonous contribution from weathered residues from the surface. These residues were transported into the cave by episodically flooding events. The age of the loamy cave sediments is not exactly known, but BURGER et al. (1993) assume that they were formed during the Quaternary. HINKELBEIN (1991) determined the age of sediments in another cave and he came up with an age of the glacial period “Würm” ice age.

### 4.2.4 Determination of the Gravimetric Water Content

The water content (ω) is determined by drying the wet sample at 105 °C until a constant dry weight is achieved. To calculate the water content, the following formula was used:

$$\omega = \frac{m_w}{m_d} \times 100\% \ [\%] \qquad [4.1]$$

where $m_w$ denotes the mass of water [M] and $m_d$ the mass of the dry sample [M].

### 4.2.5 Content of Organic Carbon

To determine the content of organic carbon ($C_{org}$) the sample was first dried (105 °C), pulverised, and decalcified. The analysis of $C_{org}$ was performed with an elemental analyser Vario EL (Hanau, Germany). The sample has been combusted at temperatures of 950 °C or rather 1150 °C under a constant oxygen flow. Finally the $CO_2$ was measured in a downstream thermal conduction detector. All $C_{org}$ values are given in percent [%].

### 4.2.6 Accelerated Solvent Extraction (ASE)

For the analysis of PAHs in soil samples an ASE 300 (Dionex, Germany) was employed. The ASE is a fully automated system, which has replaced conventional extraction methods, like Soxhlet. Samples can be extracted several times with short duration at reduced solvent volume. The pressure is 100 bar, which keeps the solvent in the liquid phase and allows the wetting of the sample even though the temperature is above the ambient pressure point (HUBERT et al., 2000; RICHTER, 2000). Acetone and toluene are the favoured solvents, because according to BANDH et al. (2000) they allow high extraction rates.

The wet samples (20–30 g) were packed in a 33 ml extracting cell with exception of the cave sediments. The latter had to be dried first, because of the high clay and silt fraction. Coagulation often happened, thus the solvent could not flow through. This problem could be avoided with dried and pulverised samples. All samples were extracted with acetone first, because acetone is miscible with water and mostly wet samples were used. The decision to use wet samples was made due to the possibility of cross contamination during drying and adsorption of gas phase PAHs onto dry mineral surfaces. After the first extraction step with acetone, which also removes the water from the sample, a second extraction with a stronger solvent, toluene, was performed. The employed extraction parameters can be seen in Table 4.1.

Subsequent to the extraction, the surrogate standard was added to both acetone and toluene extracts. Afterwards, the procedure for the two kinds of extracts differed. The further processing of the acetone extracts was a liquid-liquid-extraction: Water (2 L) and cyclohexane (10 mL) were added to the acetone extract and subsequent to this the bottles were shaken for one hour and left in the dark for another 24 hours for phase separation. Then the cyclohexane was withdrawn and evaporated with a nitrogen stream up to ~ 150 µL. The rotation evaporator and if necessary the nitrogen stream was used to minimize the toluene extract to the same amount. Finally, they were measured with GC-MS (please refer to Chap. 3). The dry mass of the analysed sample was determined using the water content. The method detection limit for soils is around 20 µg $kg^{-1}$.

**TABLE 4.1:** Parameters of the extraction using ASE.

| **Extraction Parameter** | **M11** | **M12** |
|---|---|---|
| solvent | acetone | toluene |
| duration | 2 x 10 min | 2 x 10 min |
| pressure | 100 bar | 100 bar |
| temperature | 100 °C | 150 °C |

Because of the co-extraction of natural organic substances, it was necessary to clean up the samples with a column-chromatography (Chap. 3).

### 4.2.7 Sorption Isotherms

The dried and pulverised samples were weighted into vials (0.02-0.1 g). Millipore water and the stock solution (Phe) were added. After that the samples were shaken for one week at a temperature of 20 °C in the dark, to reach the sorption equilibrium. According to KLEINEIDAM et al. (2002) seven days are sufficient to establish sorption equilibrium with pulverised samples. After centrifugation the water was extracted and spiked with Nap as the surrogate standard, cyclohexane was added. Finally, the sample was shaken again, the cyclohexane was extracted and measured with the GC-MS (Chap. 3). Reference samples were treated the same way, but without stock solution. For more details please refer to WANG (2006).

For the cave sediments the triplicate investigation showed large concentration fluctuations, indicating little sorption or technical problems such as coagulation during the sorption isotherm experiment. To avoid this phenomenon, sodium diphosphate was added. However, this anticoagulation agent hampered sedimentation and the water could not be separated from the sediments. Additionally, it was not possible to filter the sample, because the filter clogged immediately. In a further attempt, the cave sediment samples were treated with sodium azide, to minimise growth of microorganisms. The results of this treatment were satisfying; consequently there must have been some biodegradation during the initial experiments.

The sorption data were fitted by the Freundlich model, which allows the description of nonlinear sorption. The combination of pore-filling/adsorption and partitioning in a wide range of geosorbents can be fitted very well by the Freundlich model (GRATHWOHL and RAHMAN, 2002):

$$C_s = K_{Fr} C_w^{1/n} \qquad [4.2]$$

$K_{Fr}$ and 1/n are the Freundlich sorption coefficient [M $M^{-1}$] and the exponent [-], respectively. The exponent indicates the degree of linearity. If it equals 1, then sorption is linear. In this case, partitioning dominates the sorption process rather than pore-filling (adsorption). The other way round, a low Freundlich-Exponent and therefore a high non-linearity of sorption, is generally attributed to adsorption (pore-filling) rather than absorption (partitioning). Additionally, the isotherms were normalised to the subcooled liquid solubility $S_{sub}$.

$$C_s = K_{Fr}^{*}\left(\frac{C_w}{S_{sub}}\right)^{1/n} \quad [\mathrm{M\ M^{-1}}] \qquad [4.3]$$

where $S_{sub}$ is the subcooled liquid solubility [M $L^{-1}$]. In this work the value of SCHWARZENBACH et al. (1993) was taken, which is $S_{sub} = 6.17$ mg $L^{-1}$.

The distribution coefficient $K_d$ was determined by calculating the mass balance:

$$K_d = \frac{C_s}{C_w} = \frac{(X_{tot} - X_w)V_w}{X_w m_d} \quad [\mathrm{L^3\ M^{-1}}] \qquad [4.4]$$

in which $X_{tot}$ denotes the total solute mass [M], $X_w$ the mass in water after equilibration and $V_w$ the volume of water [$L^3$].

Furthermore, $K_d$ was normalised to the organic carbon content, to calculate the $K_{oc}$:

$$\log K_{oc} = \log K_d - \log\left(C_{org}/100\right) \qquad [4.5]$$

### 4.2.8 Quality Assurance

The recovery rate for all soil samples for Ace d10 ranged between 18 % and 71 % and for Phe d10 between 20 % and 65 %. There was a trend towards lower recoveries for Nap recovery rates increased with the decreasing solubility of the PAHs, what means that Per and Chr showed the highest recovery. The low recovery rate is due to the incomplete transfer of PAHs from the water-acetone mixture into cyclohexane. Furthermore, the extracts were cleaned up several times, so there was also a loss of PAHs. These losses were compensated by the employed surrogate standard.

## 4.3 Results and Discussion

### 4.3.3 Soil Samples

The concentrations of ∑PAHs from the top soils, including the agricultural soils, ranged between 200 and 20000 µg $kg^{-1}$. All samples from the deeper horizons showed general lower concentrations up to 3000 µg $kg^{-1}$. Data are listed in appendix B.

#### 4.3.3.1 Vertical Transport of PAHs

A trend of decreasing fraction of the HMW-PAHs showed up with deeper soil horizons. The PAHs with 4-6 rings dominate the profiles in the top soils. In deeper horizons the LMW-

PAHs get more relevance, actually in the deepest horizon, where Fln and Phe represent 60 % of ∑PAHs (BP VK3). In this case bioturbation is not responsible, because this process is not selective. It transports all PAHs independent of their solubility. Especially, the LMW-PAHs are transported because of their lower octanol-water-partitioning coefficient ($K_{ow}$) and their higher solubility (S). This could indicate that transport with the seepage water occurs. However, a particulate transport should not be neglected, because BbF is also represented in these deeper horizons. Transport processes are also discussed in Chap. 5, in which the column and leaching tests with the soil samples are presented. It should be kept in mind that, if concentrations of PAHs are low (in the range of the detection limit), the distribution patterns could be an artefact because of cross-contamination.

The portion of Phe also increased with increasing depth. That means that Phe is the most dominating of the PAHs concerning transport processes.

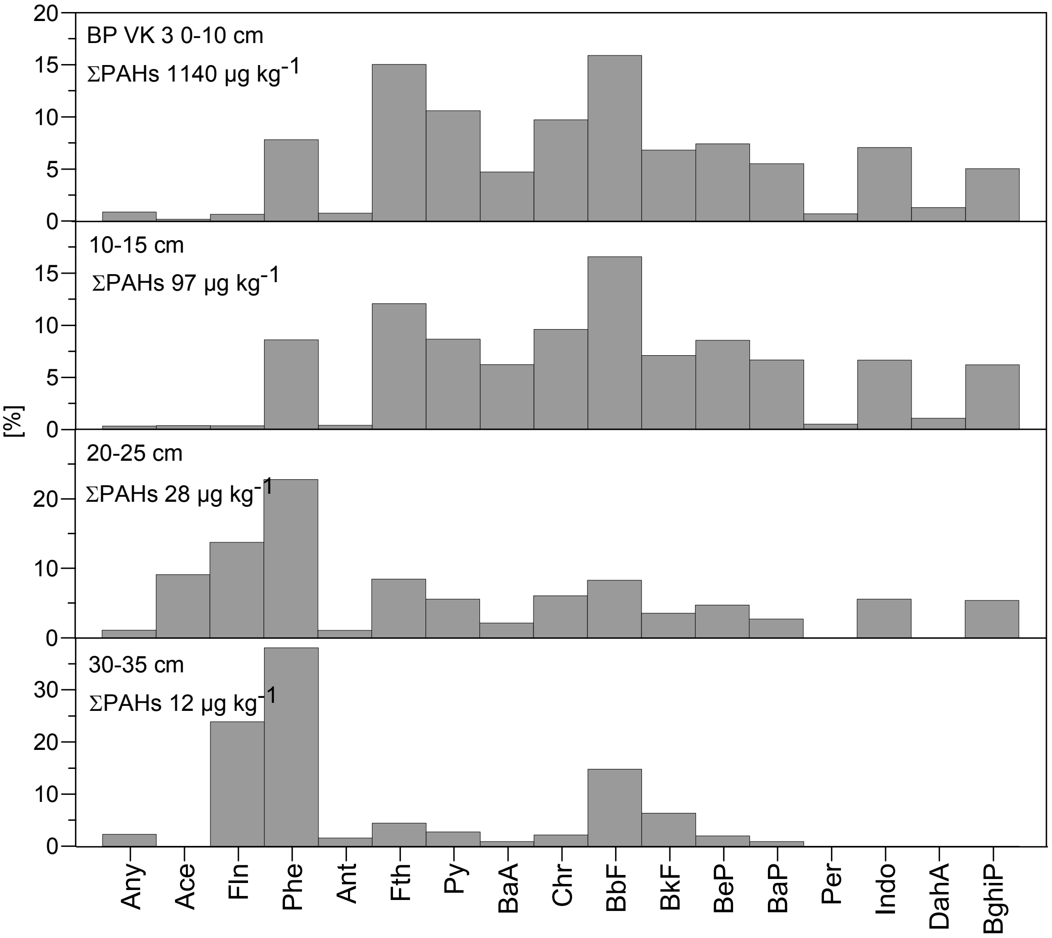

**FIGURE 4.1:** Distribution pattern of PAHs in different depths of the soil profile, BP VK 3 (0-35 cm).

### 4.3.3.2 Distribution Pattern

The distribution patterns of the top soils and the agricultural soils showed almost the same fractions of Fth (15 %), BbF (13 %), Py (10 %), Chr (9 %) and Phe (9 %) (averages, n=24). Phe was dominant in atmospheric deposition (Chap. 3), but it showed lower fractions in the soils. This can be due to biodegradation, volatilisation, or leaching (DOICK et al., 2005). The LMW-PAHs and the intermediate PAHs have a prevailing position in the distribution pattern of the deeper horizons (averages, n=14), Phe (17 %), BbF (12 %), Fth (10 %), Fln (8 %) and Py (7 %). However, the concentrations are rather low, so a cross-contamination could be also a reason for this kind of distribution.

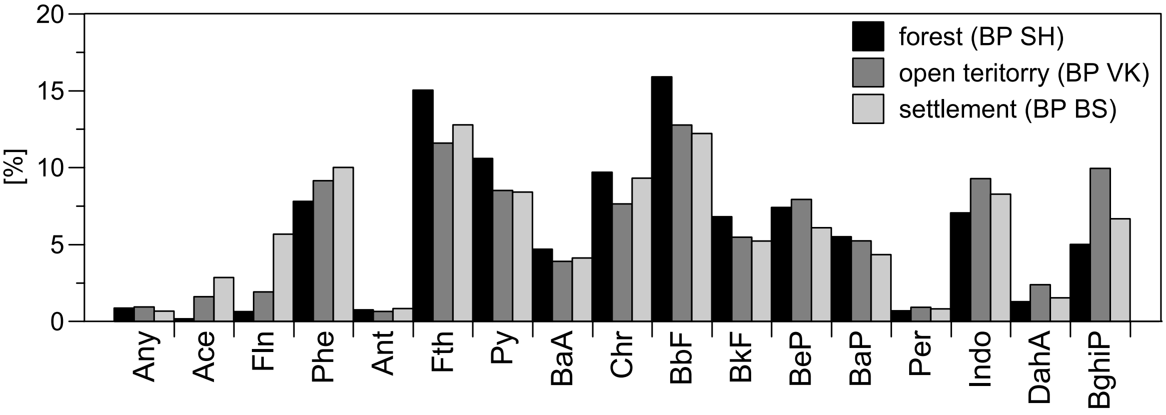

**FIGURE 4.2:** Distribution pattern from top soils of different compartments, open territory, forest and settlement.

A comparison of top soils from different compartments did not show any significant differences in the distribution pattern. This indicates same sources and input process for all soils. According to COLOMBO et al. (2006) and YUNKER et al. (2002) Fth/(Fth+Py) and BaP/(BaP+Chr) ratios lower than 0.4 and 0.2 indicate petrogenic sources whereas values higher than 0.5 and 0.35, respectively, indicate combustion processes. All soil samples of this work plot in the pyrogenic field (e.g. vehicle emission, household heating, Fig. 4.2). Main input is by atmospheric deposition; only in one case can sewage sludge application onto agricultural land not be excluded.

The Indo/(Indo+BghiP) ratio gives information on sources, because this ratio is least altered by photooxidation or other transformation processes during atmospheric transport (ACEVES and GRIMALT, 1993; OLIVELLA, 2006). The main ratios are 0.56–0.62 for coal and wood soot and 0.52 for kerosene combustion (SICRE et al., 1987). The values found in the soils of this study, ranging between 0.47–0.63, are typical for fossil fuel combustion.

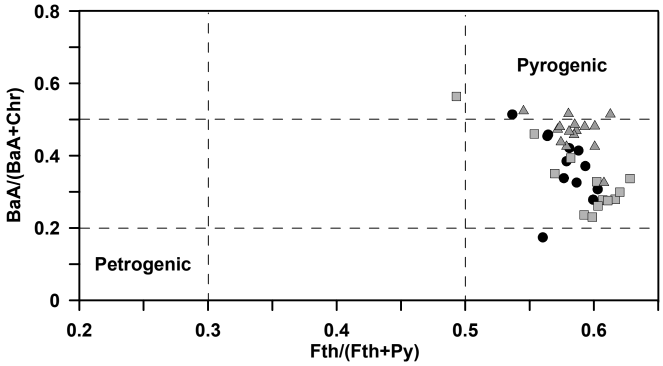

**FIGURE 4.3:** Pyrogenic and petrogenic derivation of PAHs on the basis of Fth/(Fth+Py) and BaA/(BaA+Chr) ratios.

It is possible that the agricultural soil with the highest concentration (~20 mg $kg^{-1}$) was amended by sewage sludge. BUSSETTI et al. (2006) found concentrations of their sewage sludge (Italy) in the range of 1.4 to 1.3 mg $kg^{-1}$. SÁNCHEZ-BRUNETE et al. (2007) found values for the area from Madrid in the range of 310 to 5120 mg $kg^{-1}$. However, if the sewage sludge was deployed on a regular base, enrichment could occur.

### 4.3.3.3 Historical Deposition Rates

The PAHs inventories in soils can be linked to the historical deposition rates, if it is proven that the PAHs burdens in soils are due to atmospheric deposition. A high correlation of PAHs patterns between soils and air particles strongly points to combustion sources as dominant contributors (SIMCIK et al., 1996). The total input by atmospheric deposition can be calculated by the following equation (GOCHT, 2005):

$$\mathrm{Inv} = \int \mathrm{E} \cdot \mathrm{Ddt} \quad [\mathrm{M\,L^{-2}\,t^{-1}}] \qquad [4.6]$$

D indicates the deposition rate [M $L^{-2}$ $t^{-1}$] and E the enrichment factor for different time periods. E is given by E(t) = 0.09, t < 1880; E(t) = 0,022t – 41.28, 1880 < t <1965; E(t) = 79.424 -0.0394t, 1956 < t <1990; E(t) = 1, t > 1990 (GOCHT, 2005). For the yearly deposition rate the value 86 µg $m^{-2}$ $a^{-1}$ was taken from the atmospheric deposition (Chap. 3).

In the time period between 1850-2006 the inventory linked to today's deposition was 1 2.4 mg $m^{-2}$ in the whole Blautopf Catchment. The year 1850 was taken as beginning of this estimation, because earlier records are not available.

### 4.3.3.4 PAHs Inventories

In order to compare the PAHs loading of the different soil compartments, inventories were calculated according to the following equation (SIMCIK et al., 1996):

$$\mathrm{Inv} = \Sigma\left(\mathrm{C_S} - \mathrm{C_B}\right)\rho_{\mathrm{B}} \cdot \mathrm{d} \quad [\mathrm{M\,L^{-2}}] \qquad [4.7]$$

where Inv is the PAHs inventory, $C_S$ the concentration of ∑PAHs in [M $M^{-1}$], $C_B$ the background concentration, $\rho_B$ the bulk density [M $L^{-3}$] and d the depth of each increment [L]. SIMCIK et al. (1996) did this calculation for a historical record in sediments, what means the $C_B$ refers to background values before the industrialisation (~1800). With the assumption that the concentration of PAHs increased significantly only with the beginning of the Industrial Revolution, $C_B$ was neglected here.

The inventories of PAHs have been calculated for five soil profiles in the catchment area (BP BS, BP SH, BP VK 1-3). At the base of the valley, the soil was thickest, whereas at the plateau it was thinnest. The inventories showed some difference. They ranged between 82 and 204 mg $m^{-2}$ depending on location. However, if only the top soils were considered, the inventories varied between 26 and 171 mg $m^{-2}$. In comparison to the literature these values are rather high. GUGGENBERGER et al. (1996) found PAHs inventories in the range of 35-105 mg $m^{-2}$ in a rural area of Southern Germany. It should be considered that for all soils the same bulk density was estimated and the classification of the different horizons was sometimes very difficult. Additionally, the investigated area is agricultural land which can also receive PAHs from other sources than atmospheric deposition, such as sewage sludge application. In comparison to the estimated inventory of the historical PAHs record the observed values are higher. This indicates that PAHs accumulate in soils and no significant degradation, transport, or volatilisation takes place.

Calculated inventories for the PAHs substances BaP (3-11 mg $m^{-2}$) and BeP (6-14 mg $m^{-2}$) showed similar results; however, the values for BaP were lower in all profiles. The ratio BeP:BaP was in the range of 0.4 and 0.8, whereas the sample BP VK 2 showed the lowest one. According to SPITZER & KUWATSUKA (1993) these two substances were emitted in a ratio of 1:1. This ratio was also affirmed in the atmospheric deposition of this area. This means that the lower values of BaP would indicate a favoured degradation or transport process in the soil. GOCHT (2005) found also different ratios in the Black Forest. Nonetheless, he reported that the degradation of BaP would be a discrepancy to the hypothesis that particle bound PAHs are not bioavailable and thus not able to be degraded.

Inventories rather than concentrations are used to compare the storage of pollutants in the different soil compartments, because the influence of different bulk densities of the soil horizons can be eliminated by means of these calculations. This is important since bulk densities of humic layers and top soils vary within a factor of 10 or even higher, and these two compartments are the most important ones with respect to storage of PAHs in rural soils. Due to the huge catchment size (165 $km^2$), some simplifications were applied. CHEN et al. (2006) modified an equation to calculate the PAHs burden in a specific area:

$$\mathrm{Inv} = \Sigma C_S \cdot A_s \cdot d \cdot \rho_B \qquad [4.8]$$

where $A_s$ is the area [$L^2$]. It is very difficult to derive the exact values, because the area is very large and it is not possible to know for example the depth, concentration, bulk density of the top soils in the whole area. The results of this calculation can be found in Table 4.2. Additionally, values from Bund-Länder-Arbeitsgemeinschaft Bodenschutz (2003) were taken for this calculation. They determined background values for specific areas (e.g. "Baden-Württemberg") for the same ∑PAHs as in this study. They give values for the different types of top soils: Farmland: 193 µg kg$^{-1}$, grassland: 255 µg kg$^{-1}$, forest: 254 µg kg$^{-1}$ and 1147 µg kg$^{-1}$ for the litter in the forest. These background data were additionally used to compare it with my own measurements, because the soils in the catchment varied a lot and PAHs in litter was not determined. In both calculations, the depth of the top soils was estimated to be approximately 0.2 m and $\rho_B$ with 1.5 g cm$^{-3}$. The land use is the same as in Chap. 3, only the open territory was divided into farmland (50 %) and grassland (11 %) according to Köberle (2005). The deposition of POPs from the atmosphere to forest soils has been shown to be higher than to non-forest soils by several workers (Horstmann et al., 1997). This finding was considered by the litter values for the area covered with forest (only Bund-Länder-Arbeitsgemeinschaft Bodenschutz calculation). It was not possible to distinguish between deciduous and coniferous forests. The burden of PAHs for the whole catchment area based on own results is 40 kg and based on the Bund-Länder-Arbeitsgemeinschaft Bodenschutz (2003) values is 28 kg. If these values are converted back to 0.17 mg m$^{-2}$, then it is obvious that the values are too small in comparison to the results of the soil and historical inventory.

**TABLE 4.2:** Inventory of PAHs in the top soils of the Blautopf Catchment.

| | Land use [%] | Area [km$^2$] | $\Sigma$PAHs [µg kg$^{-1}$] | Storage [kg] |
|---|---|---|---|---|
| settlement | 8 | 13 | - | - |
| grassland | 11 | 18 | 564 | 3.1 |
| farmland | 50 | 83 | 1300 | 32.2 |
| forest | 31 | 51 | 314 | 4.8 |
| total | 100 | 165 | | 40.1 |

### 4.3.4 Cave Sediments

The concentrations of ∑PAHs for the loamy sediments came up to 117 µg kg$^{-1}$ with a mean of 55 µg kg$^{-1}$. Generally, these concentrations are very low. This is due to the low amount of organic matter in the sediments, as well as the dependency on the seepage water including small particles, as the more or less the only path way of pollutants. The average (n=4) of the distribution pattern differs from the top soils, because Phe (17 %), Fth (12 %), BbF (10 %), Py (9 %) and Indo (8 %) are the dominating substances. The whole distribution pattern (Fig. 4.4) shows that particulate transport plays a major role due to the high concentrations of HMW-PAHs.

SIMMLEIT and HERRMANN (1987) assumed that the upper 2 m of a karst system are the most effective pollutant sinks. This hypothesis can be confirmed considering the results of this study, because in the top soils the highest contents of contaminants could be determined. In contrast, the concentrations in the caves were rather low and they do not give evidence of any displacement of PAHs. Furthermore, the epikarst zone and rock matrix could be buffer zones for POPs. This subject will be discussed in Chap. 6 and 9 in connection with the seepage water and stable isotope investigations.

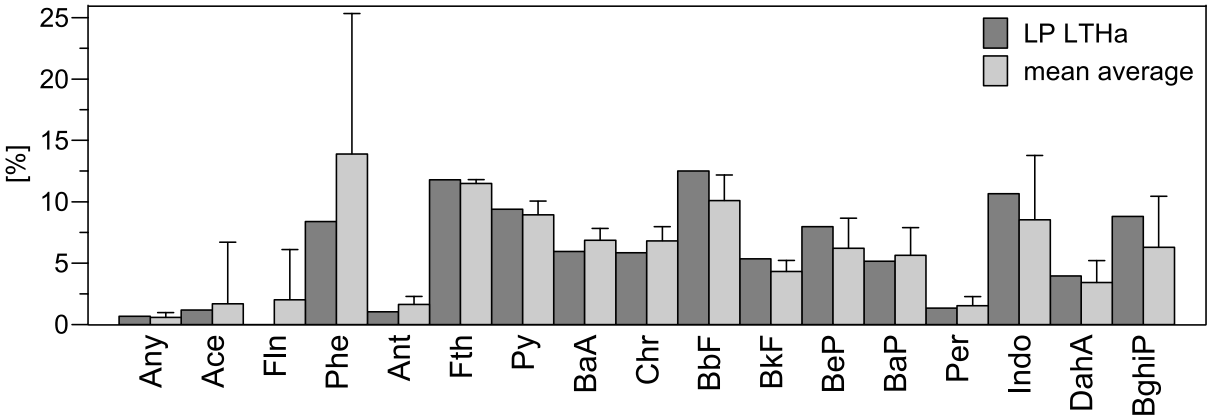

**FIGURE 4.4:** Distribution pattern of PAHs in the cave sediments (LP LTHa +b, LP SH a + b) (average, n=4).

### 4.3.5 Sorption Isotherms

The sorption of pollutants to soils is a main factor controlling the fate and transport in the environment. The sorption batch experiments for different top soils and one cave sediment show that the $K_{Fr}$ values (Phe) of all top soils are more or less constant and vary in the range of 2.30 and 2.67. Only the cave sediment shows a clearly different result with $K_{Fr}$=-0.06 mg kg$^{-1}$ (L mg$^{-1}$)$^{1/n}$. The Freundlich exponent 1/n ranged between 0.7–1.1 for all samples; this indicates that the sorption isotherms for the different soils are almost linear. Thus the partitioning process is dominant (KLEINEIDAM et al., 2002; PAN et al., 2006).

The $K_{oc}$ was calculated using equation 4.5 and the $K_{oc}$* based on the subcooled liquid solubility (6.17 mg L$^{-1}$ SCHWARZENBACH ET AL., 1993). All results are presented in Table 4.3. Usually sorption increases with higher $f_{oc}$ values. The $K_{Fr}$ results and the different normalisations are shown in Fig. 4.5.

The cave sediment (LP SH b) showed a very low $K_{Fr}$ indicating only very low sorption capacity for PAHs. This was expected, because the organic matter is very low as well.

**TABLE 4.3:** Freundlich parameters of the sorption isotherms for phenanthrene. The unit equivalent parameters are marked with *.

| Freundlich parameter | BP LTH Sp | BP GH Sei | BP GH Tie | EGBO 10 | LP SH b |
|---|---|---|---|---|---|
| log $K_{Fr}$ [mg kg-1 (L $mg^{-1})^{1/n}$] | 2.49 | 2.58 | 2.30 | 2.67 | -0,06 |
| 1/n [-] | 0.810 | 0.743 | 0.722 | 1.071 | 0.701 |
| $r^2$ [-] | 0.998 | 0.998 | 0.998 | 0.962 | 0.970 |
| $f_{oc}$ [-] | 0.052 | 0.052 | 0.022 | 0.024 | 0.002 |
| log $K_{oc}$ [L $kg^{-1}$], $C_w$=0.1 mg $L^{-1}$ | 3.96 | 4.12 | 4.23 | 4.22 | 0,24 |
| log $K_{oc}$ [L $kg^{-1}$], $C_w$=0.001 mg $L^{-1}$ | 4.34 | 4.63 | 4.79 | 4.08 | 0.84 |
| | with $C_w$ normalised to the subcooled liquid $S_{sub}$ | | | | |
| log $K_{oc}$* [mg $kg^{-1}$], $C_w$=0.1 mg $L^{-1}$ | 3.32 | 3.53 | 3.66 | 3.37 | 2.42 |
| log $K_{oc}$* [mg $kg^{-1}$], $C_w$=0.001 mg $L^{-1}$ | 3.70 | 4.04 | 4.22 | 3.23 | 3.02 |

The sorption data allow the calculation of the concentration needed to exceed the German precaution value in seepage water. For this estimation the limit for drinking water ($C_W$=0.2 µg $L^{-1}$) and the calculated distribution coefficients of the isotherms were taken to get the threshold concentration ($C_{c,tv}$) in the soil:

$$C_{c,tv} = K_d \cdot C_w \qquad [4.9]$$

For each soil, for which the sorption isotherm was determined, there was also done a leaching test. These results are described in the next chapter.

**TABLE 4.4:** Estimated $K_d$ values at $C_w$= 0.001 mg $L^{-1}$ and threshold concentrations.

| | BP LTH Sp | BP GH Sei | BP GH Tie | EGBO 10 |
|---|---|---|---|---|
| ①$K_d$ [L $kg^{-1}$] | 1137 | 2222 | 1365 | 284 |
| ②$K_d^a$ (Allan-King) | 3403 | 2985 | 1469 | 1223 |
| ③$K_d^b$ (Karickhoff) | 5246 | 3997 | 2118 | 1628 |
| ①$C_s$ [µg $kg^{-1}$] | 58 | 130 | 106 | 26 |
| ② $C_s$ | 173 | 174 | 114 | 111 |
| ③ $C_s$ | 52686 | 30023 | 2103 | 4204 |
| $C_{s,act}$ | 39 | 32 | 37 | 3241 |

[a] calculated according to Allen-King et al. (2002)
[b] calculated according to Karickhoff et al. (1979)

Based on the threshold concentration and $C_{s,act}$ the calculation of the time needed to reach the threshold concentration is possible (Gocht, 2005):

$$t_{tv} = \frac{\left(C_{c,tv} - C_{s,act}\right) \cdot d \cdot \rho_b}{D} \qquad [4.10]$$

whereas $t_{tv}$ is the time to reach the threshold concentration [t], $C_{c,tv}$ the threshold concentration [M $L^{-3}$], $C_{s,act}$ the actual concentration in the soil [M $M^{-1}$] and D the deposition flux [M $L^{-2}$ $t^{-1}$]. This estimation is based on equilibrium condition.

Depending on the $K_d$ value the threshold concentration will be attained in more than 64 years.

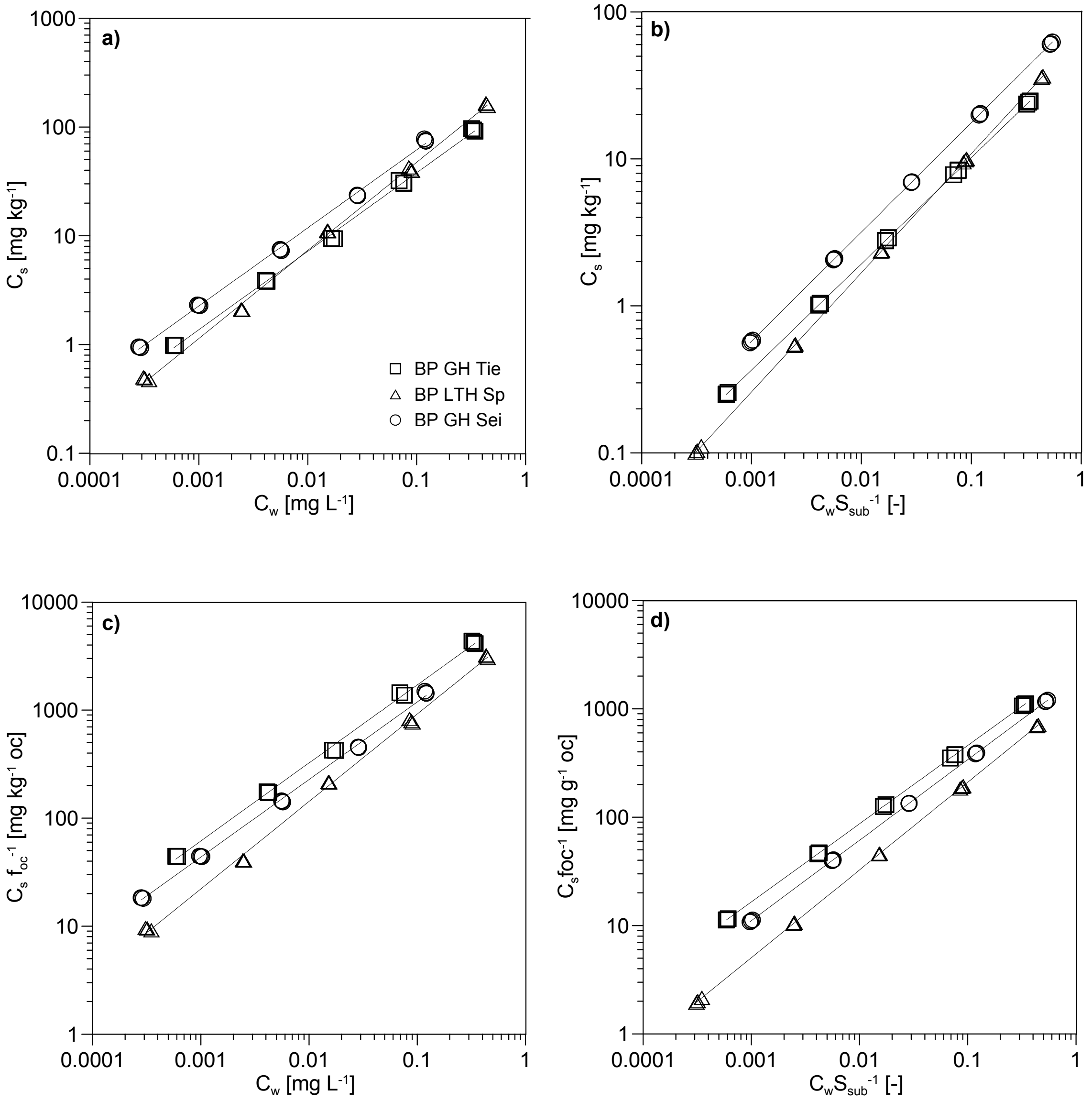

**FIGURE 4.5:** Freundlich sorption isotherms for different top soils. a) not normalised, b) normalised to $S_{sub}$, c) normalised to $f_{oc}$ and d) $S_{sub}$ and $f_{oc}$ normalised. Note the different scales.

## 4.4 Summary

Soils are an important factor controlling the storage, fate and transport of PAHs. Different kinds of soils have been investigated and they show all similar results.

- As found in other studies a main result in this investigation was that PAHs accumulate in the top soils of the Blautopf Catchment. Concentrations of the soils are partly fairly high; this gives evidence of the good storage capacity of the soils, especially of the top soils. Sorption is mainly due to partitioning processes.
- The distribution patterns in soils and atmospheric deposition are almost equal, which means the atmosphere is the main supplier of PAHs to the soils. This fact is important for calculating the input of PAHs into the catchment.
- In the loamy sediments of the caves almost no PAHs were found. This indicates that there are no significant transport processes into the deeper parts of the Blautopf Catchment. PAHs are mainly stored in the top soils and not significantly released into the seepage water and thus not accumulated in the cave sediments.

These results suggest that release and transport of dissolved PAHs in seepage and groundwater in this karst system is not significant.

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# CHAPTER 5

# DESORPTION OF PAHS (COLUMN AND LEACHING TESTS)

**Abstract**

Desorption of polycyclic aromatic hydrocarbons (PAHs) from typical soil samples of the "Schwäbische Alb" was investigated using the accelerated solvent extractor (ASE) and column tests. Leaching of PAHs showed a strong dependency on temperature, as well as on content of organic matter. With increasing temperature and DOC the concentration of PAHs in the eluate also increased. Furthermore, it was found that with higher organic content in the soil samples desorption was less efficient. The column test showed that up to 300 years would be needed to leach the total mass of PAHs from the soils under natural conditions. This indicates that the PAHs accumulate in the soils, but are not released in high amounts.

**Keywords:** column test, soils, karst area, desorption, leaching, accelerated solvent extractor

## 5.1 Introduction

PAHs accumulate in soils and sediments, but they can get released and transported with the seepage water into the groundwater. The controlling parameter for this process is the $K_d$ value, which is the distribution coefficient between the concentration in the solid and the water phase. Other important factors that control the transport of PAHs are suspended particles, colloids, and the content and type of organic matter (OM) in these materials. The latter involves all dead plant and animal substances which are in and on the mineral soil, as well as their derivatives (SCHACHTSCHABEL et al., 1998). OM appears both as particulate matter and as dissolved organic matter (DOM). DOM is defined as colloidal matter < 0.45 µm. According to PETRUZELLI (2002), organic matter may interact with PAHs by various mechanisms, which include physical and chemical adsorption, hydrolysis and others. Thus, DOM (fulvic and humic acids) can act as a carrier for pollutants (TOTSCHE et al., 1997). The sorption of PAHs to DOM follows mostly the lipophilicity ($K_{ow}$, octanol-water partitioning) of the compounds (AKKANEN et al., 2005).

To estimate the mobility of PAHs, column and leaching tests were performed. For this purpose representative soil samples of the investigated study area were chosen. In Chap. 4 it could be shown that a high content of PAHs occurs in top soils. Now the question is: Can PAHs theoretically be released and enter the seepage and groundwater? If this happens in the laboratory, it likely occurs in the field as well.

## 5.2 Materials and Methods

### 5.2.1 Elution Method ASE

The desorption behaviour of PAHs from typical soil samples was examined using an ASE technique. Eight temperature steps from 25 ± 3 °C till 100 °C were sequentially utilised. Pure deionised water was chosen for leaching. With increasing temperature the concentration of PAHs increases because sorption decreases (JOHNSON and WEBER, 2001; REZA et al., 2002). Due to the higher temperature, the water polarity decreases and thus the dielectric coefficient does as well; this in turn increases the solubility of PAHs.

To avoid clogging in the ASE cells (100 mL), the freeze dried soil samples were mixed with silica sand at a ratio of 2:1. Two cells were used in parallel and the extracts of each temperature step were combined in one bottle. This was done because of the low concentration of PAHs in the leachates. The extraction time of 99 min was selected to reach equilibrium between the solid and the aqueous phase. To ensure that equilibrium conditions are achieved, one temperature step was implemented with 30 and 99 min. In case of the same concentrations, the conditions for equilibrium were given.

**TABLE 5.1:** Parameters of the ASE for water extraction.

| Extraction Nr. | Solvent | Temperature [°C] | Time [min] |
|---|---|---|---|
| M1 | water | 25 ± 3 | 30 |
| M2 | water | 25 ± 3 | 99 |
| M3 | water | 40 | 99 |
| M4 | water | 47 | 99 |
| M5 | water | 53 | 30 |
| M6 | water | 53 | 99 |
| M7 | water | 64 | 99 |
| M8 | water | 75 | 99 |
| M9 | water | 87 | 99 |
| M10 | water | 100 | 99 |
| M11 | acetone | 100 | 2 x 10 |
| M12 | toluene | 150 | 2 x 10 |

After aqueous leaching at the different temperatures, two solvent extractions were done to get the total amount of PAHs in the solids for calculating the mass balance. After the extraction a surrogate standard was added to all extracts (Chap. 3). Cyclohexane was added to the water (M1-10) and acetone (M11) samples; afterwards the bottles were filled up with Millipore water and shaken for one hour. Then they were stored in the dark to establish the separation of the different phases. After at least 24 hours the supernatant cyclohexane was sampled, reduced to ~150 µL under a gentle stream of nitrogen and analysed using GC-MS. The toluene extracts were minimized to ~150 µL using the rotation evaporator and the nitrogen stream afterwards. Before the GC-MS measurement an internal standard (Fth-d10) was added into all samples.

### 5.2.2 Column Test (DIN V 19736)

Column tests are suggested by the German "Bundesbodenschutzverordnung" (BBodSchV) to determine leaching of pollutants. In Fig. 5.1 the set-up of a column test is given. The sample material is packed into a glass column between two filter layers of silica sand. To eliminate air bubbles and to achieve a homogenous flow and a high reproducibility, the sample was filled in underwater-saturated conditions. The lower silica filter assures homogenous flow through the sample. The upper one avoids the flush out of coarse particles that could clog the stainless steel tubing, leading the eluate into the sampling bottle. The sampling bottle contains 5 mL cyclohexane and the surrogate standard. This way of doing leads to a fast transfer of PAHs into the solvent.

For the elution deionised water mixed with sodium azide (10 mg $L^{-1}$) was used. This minimised the microbial degradation during the test. The flow rate was approximately 0.6 mL $min^{-1}$. Assuming a porosity of the soil samples of 30 % results in a flow velocity of the seepage water of approximately 1 m $d^{-1}$. The pore volume was displaced 7 times per day. Samples were taken on a regular base after 24 and 48 hours for 13 days. To determine the DOC and the turbidity, control samples consisting of 30 mL were taken as well.

The used soil samples can be identified with the following labelling: SV 0 = blank (silica sand), SV 1 = BP LTH Sp, SV 2 = BP GH Sei, SV 3 = BP GH Tie and SV 4 = EGBO 10.

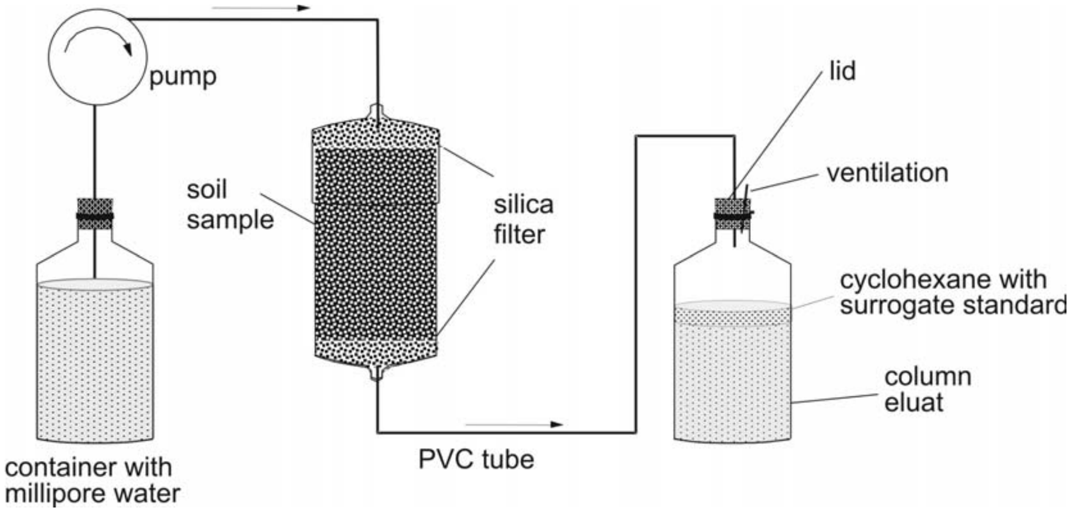

**FIGURE 5.1:** Schematic assembly of the column test.

### 5.2.3 Desorption Thermodynamics of PAHs

On the basis of the equilibrium established in the ASE leaching test the isosteric heat of desorption ($\Delta H_{des}$) can be calculated with the following equation (Van't Hoff plot):

$$-\Delta H_{Des} = R \frac{d \ln\left(\frac{1}{K_d}\right)}{d\left(\frac{1}{T}\right)} \quad [5.1]$$

where $\Delta H_{Des}$ denotes the molar heat of desorption [kJ $mol^{-1}$], R the gas constant [kJ $K_{oc}^{-1}$ $mol^{-1}$] and T the temperature [K]. For this calculation the values in the temperature range of 53-100 °C were used, because at lower temperatures the measured concentrations were below the detection limit. The low concentrations of PAHs in the soil samples avoided partially also the calculation of $\Delta H_{Des}$ at the higher temperatures.

### 5.2.4 Determination of DOC

The DOC was determined using a high-temperature-TOC-analyser (Elementar, Hanau, Germany). First all samples were filtrated manually with a Millipore filter having a pore diameter of 0.45 µm. Afterwards 20 mL of each sample were used for the analysis. Before the DOC could be analysed, the total inorganic carbon (TIC) was removed by fumigation (HCl) and stripping. The determination of the DOC was made by the direct-method.

### 5.2.5 DOC Correction

The concentration of PAHs depends on the amount and character of the organic carbon. Additionally, DOC can influence the concentrations of PAHs in the leachate (TOTSCHE, 2003). This effect can be accounted for the following equation:

$$\frac{C_{W,doc}}{C_W} = 1 + f_{doc} \times K_{doc} \qquad [5.2]$$

where $C_{w,doc}$ denotes the measured apparent aqueous concentration [M $M^3$], $K_{doc}$ the partitioning coefficient between water and DOC and $f_{doc}$ is the mass fraction of DOC in water. The $K_{doc}$ can be estimated from $K_{ow}$ using the following equation (PYKA, 1994):

$$\log K_{doc} = 0.937 \log K_{ow} - 0.46 \qquad [5.3]$$

where $K_{ow}$ is the partitioning coefficient between octanol and water.

### 5.2.6 Turbidity Measurement

To determine the turbidity in the aqueous leachate for the columns a turbidity meter was used (Hach, Düsseldorf, Germany). The samples were shaken for 20 seconds to resuspend the particles. Because the particles sank partially very rapidly, the measurement had to be accomplished very quickly. The turbidity values are given in FNU (Formacin Nephelometric Unit), which ranges between 0 and 4000 FNU. Before the measurement was started, the analyser was calibrated with standard solutions.

## 5.3 Results and Discussion

### 5.3.1 Leaching Test

The leaching test with the ASE showed higher concentrations with increasing temperature. The same phenomenon appeared with the DOC content in the sample. DOC was only measured for EGBO 10, because this soil sample had a higher concentration and not all of the extract was required for GC-MS analysis. Both results can be seen in Fig. 5.2. $C_w$ increased constantly with higher temperatures, whereas the DOC increased suddenly after a temperature of 64 °C was reached. $C_s$ in the case of EGBO 10 was at a temperature of 100 °C ca. 25 times higher than at 40 °C. Normally, DOC in the eluate increases with increasing temperature (ANDERSSON et al., 2000; MARTINEZ et al., 2003). In this study the different behaviour could be an effect of different structured DOC, which changes with higher temperatures.

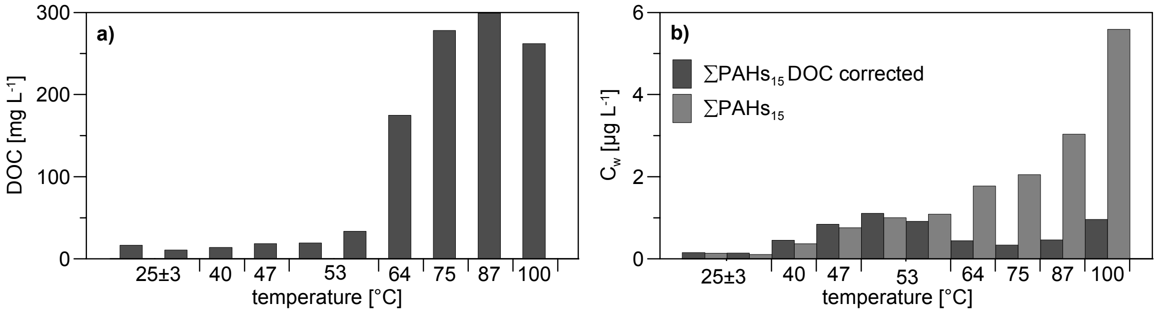

**FIGURE 5.2:** a) Temperature influence on DOC release, b) and on desorption of ∑PAHs15 (both EGBO 10).

The LMW-PAHs and intermediate PAHs dominated in all analysed samples. The distribution patterns could be divided in two different ones (Fig. 5.3). The five most important PAHs accounted for around 70 % of ∑PAHs: Phe (29 %), Fth (18 %), Py (8 %), BbF (7 %) and Any (6 %). The different distribution patterns indicate probably two transport mechanisms: dissolved and particle associated mobilisation. In GH Sei and EGBO 10 the main process was a dissolved transport, because only the LMW-PAHs and intermediates are present, whereas along GH Tie and LTH Sp the particle or more likely DOC associated transport played a major role for release of the HMW-PAHs.

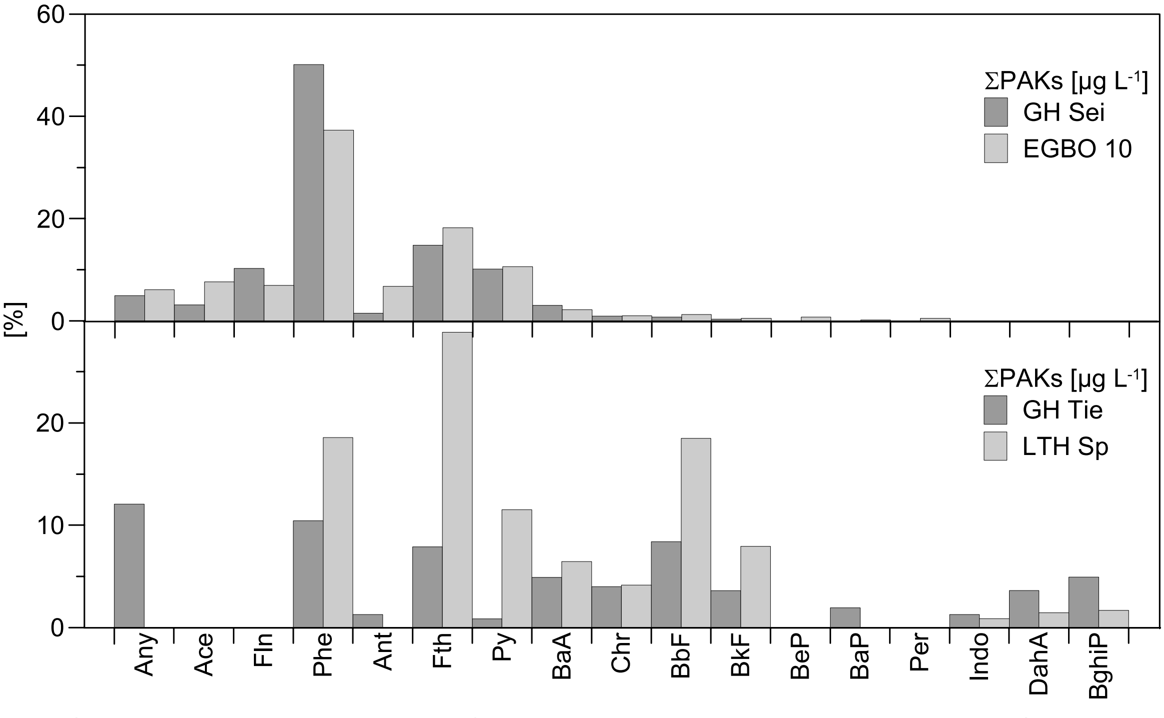

**FIGURE 5.3:** Distribution patterns of the analysed soils with the aqueous leaching (average value; ASE).

The ratio of LMW to HMW-PAHs in EGBO 10 showed a well-defined correlation with increasing temperature. At low temperatures up to 40 °C the ratio was around 14 and from 53 °C on it increased. The highest value (184) was achieved at 64 °C, afterwards it was nearly constant at 130 (Fig. 5.4 b).

For EGBO 10 a DOC correction was made to illustrate a dependency of mobilisation of PAHs by DOC. This influence is shown in Fig. 5.4. There the measured and DOC corrected values for Phe and BaA are presented. The measured data showed a clear increase with increasing temperature, but after the correction the slope vanished. This characteristic applies only for the LMW-PAHs, because the HMW-PAHs hardly dissolve in water due to their high log $K_{ow}$.

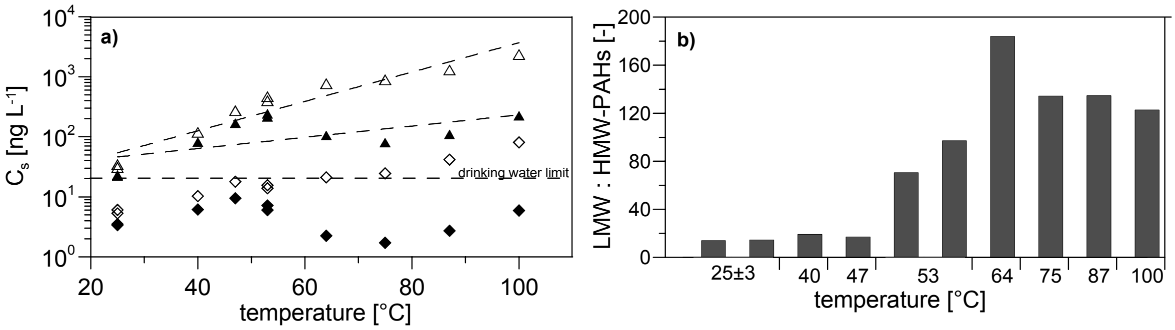

**FIGURE 5.4**: a) Measured and DOC corrected values for Phe and BaA, ▲ Phe corrected, △ Phe measured, ◆ BaA corrected, ◇ BaA measured b) shows the ratio of LMW:HMW-PAHs in dependency of the temperature (EGBO 10).

Sorption depends on the nature of organic matter; for this reason, the molar heat of desorption varies for the different materials. All calculated $\Delta H_{des}$ are given in Table 5.2.

The $K_d$-values (not shown) were greater than the ones from the sorption isotherms. These data give information about a non-linear sorption process at low concentrations.

The sample GH Sei has the highest $C_{org}$ content with 5.2 % and it shows the highest values for $\Delta H_{des}$. LTH Sp has a $C_{org}$ of 4.3 % and showed similar desorption isosteric heats. The largest problem in this investigation was that the samples did not have high (native) loadings of PAHs, with exception of EGBO 10. Phe concentrations for LTH Sp ranged between 20-140 ng $L^{-1.}$ These values are rather low. Thus, it is not possible to make any statements about desorption processes in this case.

**TABLE 5.2:** Comparison of molar heat of desorption ($\Delta H_{des}$) from the analysed samples.

| | **Any** | **Ace** | **Fln** | **Phe** | **Ant** | **Fth** | **Py** |
|---|---|---|---|---|---|---|---|
| **Sample** | **$\Delta H_{des}$** | **$\Delta H_{des}$** | **$\Delta H_{des}$** | **$\Delta H_{des}$** | **$\Delta H_{des}$** | **$\Delta H_{des}$** | **$\Delta H_{des}$** |
| EGBO 10 | -22.0 ± 7.6 | -25.5 ± 1.0 | -33.1 ± 1.3 | -36.5 ± 4.3 | -32.2 ± 0.4 | -33.1 ± 9.9 | -38.7 ± 7.3 |
| BP GH Sei | -30.7 ± 5.1 | - | -36.3 ± 1.6 | -44.7 ± 1.5 | - | -62.0 ± 3.1 | -52.7 ± 2.7 |
| BP LTH Sp | - | - | - | -21.1 ± 10.3 | - | -19.4 ± 0.5 | -19.7 ± 1.6 |
| BP GH Tie | - | - | - | -16.9 ± 6.1 | - | - | - |

### 5.3.2 Column Test

The concentrations in the eluate did not vary much and were rather constant over sampling period (Fig. 5.5). This applies in particular for the samples SV 1, 2 and 3, which stayed below the 22 ng $L^{-1}$ line. Only SV 4 showed an increase at the beginning (63 ng $L^{-1}$) followed by a steep decrease (28 ng $L^{-1}$). At the ninth day there was another peak level with 55 ng $L^{-1}$. However, there was no correlation with the DOC or the turbidity.

The blank column showed rather high concentrations with an average of 30 ng $L^{-1}$. Thus it is definitely higher as the samples SV 1-3; this can probably be attributed to contaminated silica sand and/or the column. Mainly the Phe and Fth concentrations were elevated; together they amounted for more than 50 %. As a result of the high blank values (background) it was not possible to do a blank correction.

The distribution patterns of the different soils varied a lot. An overview with the five most frequently present PAHS is presented in Fig. 5.5. A change of the patterns over time is not in evidence. There is no significant difference in SV1 + 2 concerning the distribution of LMW and HMW-PAHs. In contrast, the LMW-PAHs dominate in SV 3 + 4. It can be distinguished that the latter ones are essentially influenced by solution processes and not by particle transport. However, there is no significant release of dissolved PAHs, because the concentrations are rather low.

A comparison with the results from aqueous leaching (ASE) shows that the output of PAHs with the ASE (at a temperature of 20 °C) is in all cases higher. The ASE values are up to 60 times higher. However, the distribution patterns correlate very well.

The legal limit for BaP is never exceeded, neither in the ASE leaching (20 °C) nor in the column tests. In Blautopf Spring (Chap. 7), there is a background concentration of about 10 ng $L^{-1}$ and in the columns showed average values of 18 ng $L^{-1}$. Without the high loaded sample (EGBO 10) the average value increases to 11 ng $L^{-1}$. This result is a good agreemant between laboratory and field study.

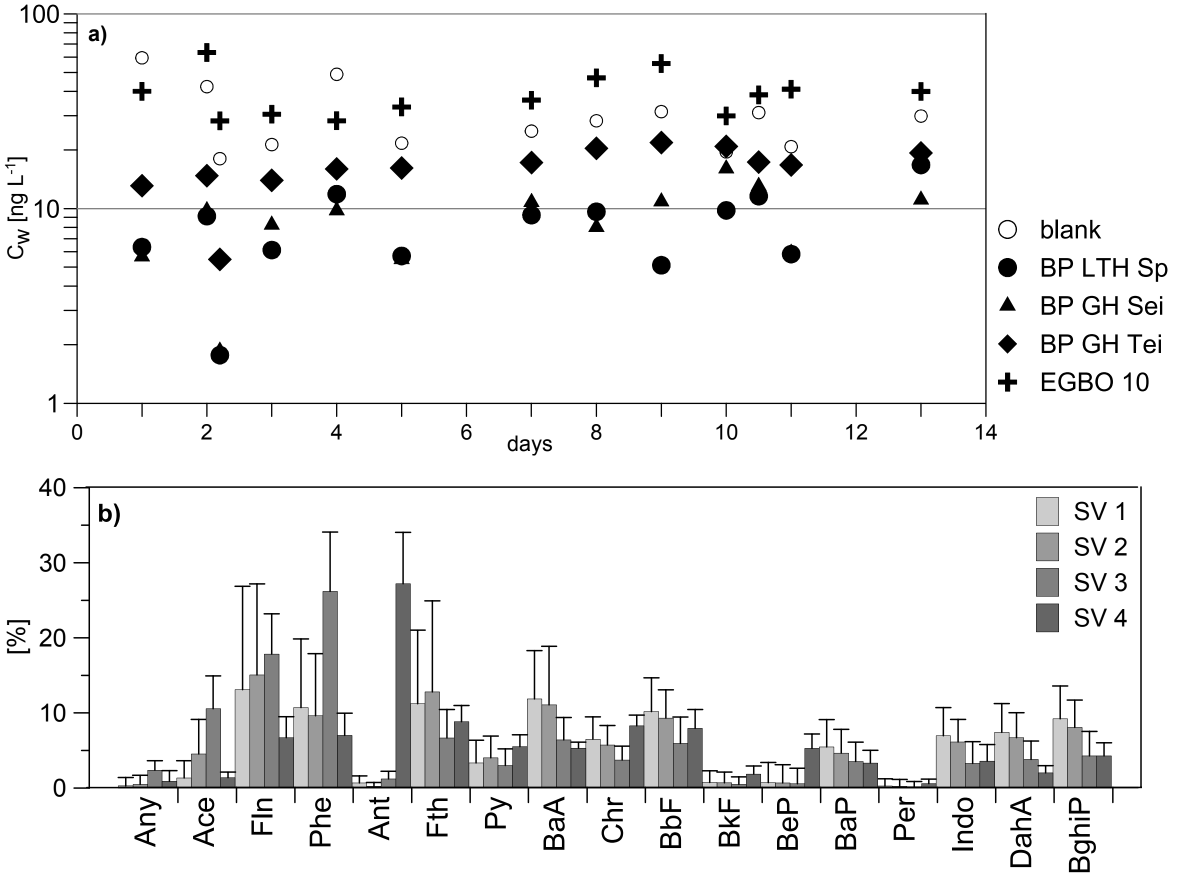

**FIGURE 5.5**: a) Results of the column test for all soils (∑PAHs), b) Average distribution patterns of PAHs in the leachate of the five columns (each n=14).

### 5.3.2.1 The Effect of DOC During the Column Test

The DOC was more or less constant during the experiment. Except for the blank, the values ranged between 1 and 10 mg L$^{-1}$, whereas SV 2 had the highest DOC content. There is no positive correlation between $C_w$ and DOC (not shown). Furthermore, a DOC correction did not cancel out the $C_w$ variations, like the peak level from SV 4. Instead it depleted only the concentrations in the range of 6-33 %.

The turbidity and consequently the particles were higher at the beginning. They decreased within three days and remained relatively constant or continued decreasing. Only SV 1 showed an increase at the end of the experiment. A correlation with the concentration of PAHs and its distribution is indeterminable. At the beginning, when particles were released, the HMW-PAHs should show a higher presence, but this, however, was not the case.

To check equilibrium, the flow velocity was increased up to ~4 mL min$^{-1}$ for about 4 h. Again, it showed no variation on $C_W$. MADLENER (2004) observed also no concentration shift with a doubled flow velocity. This gives evidence of equilibrium conditions during the investigation.

#### 5.3.2.2 Estimate of a Theoretical Breakthrough

It is interesting to know the total amount of PAHs which was leached out to calculate the (theoretical) duration of the complete decontamination of a soil sample. First the flux had to be determined by using the following equation:

$$F = L \cdot C_w \qquad [5.4]$$

where F denotes the flux [M $t^{-1}$], L the water discharge [$L^3$ $t^{-1}$] and $C_W$ the concentration in the eluate [M $L^{-3}$]. Next step is the calculation of the mass loss in the column over time to determine the duration of the whole output of the contamination. This can be done using the following equation:

$$Du = M \div F \qquad [5.5]$$

where Du is the duration of the total contaminant output [t] and M the amount of contaminants in the soil [M], respectively. The flux was determined as an average over the whole duration of the column test and the loading of PAHs was found out with the ASE.

The results for the complete output ranged between 16 and 271 years, whereupon the one with the highest contamination showed the longest period. All results are given in Table 5.3.

**TABLE 5.3**: Results from the output calculation.

| | $C_S$ [µg $kg^{-1}$] | Initial dry weight [kg] | Loading of PAHs [kg] | Flux (average n=14) [kg $d^{-1}$] | Duration of the contaminant output (average, n=14) [y] |
|---|---|---|---|---|---|
| SV 1 | 705 | 0.158 | $111.2x10^{-6}$ | $15.2x10^{-9}$ | 42 |
| SV 2 | 364 | 0.141 | $51.2x10^{-6}$ | $16.2\ x10^{-9}$ | 18 |
| SV 3 | 359 | 0.251 | $90.1x10^{-6}$ | $21.8\ x10^{-9}$ | 16 |
| SV 4 | 19963 | 0.218 | $4344x10^{-6}$ | $55.8\ x10^{-9}$ | 271 |

## 5.4 Summary

The results of this chapter confirm the findings of the prior ones; that most of the PAHs stay in the soils and are not released. The most important findings were:

- Measured concentrations of PAHs in the column test, as well as with the ASE leaching, have been rather low. The legal limit for BaP has not been exceeded.
- In the column test two different distribution patterns have been found, which give evidence of two different transport processes: dissolved and particle facilitated. However, there is still significant output at ambient temperature.

These leaching tests with typical soils of the catchment have shown that a breakthrough should not appear in near future and thus be a risk for groundwater.

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# CHAPTER 6

# NATURAL LYSIMETER - PAHS IN SEEPAGE WATER OF CAVES IN THE BLAUTOPF CATCHMENT, SOUTHERN GERMANY

**Abstract**
The “Schwäbische Alb” is one of the best-known and largest karst areas in Germany. Here we investigated the atmogenic input of pollutants into groundwater. In principal, karst aquifers have a high vulnerability for the input of contaminants, because of a thin soil layer, many sinkholes, and other direct pathways to the groundwater. PAHs as ubiquitous environmental tracers were studied in the seepage water for a two-year period. We used a passive sampler device, as well as water samples to determine the fate and behaviour of the contaminants in the vadose zone. Therefore, we focused our investigations on high-flow events such as snowmelts and thunderstorms. The concentrations of PAHs in the seepage water varied between 2 and 846 ng $L^{-1}$, whereas the higher molecular weight compounds were always found during snowmelt events. Furthermore, the transport processes were dominated by particles. This indicates that they infiltrate straight from the surface along preferential flow paths.

**Keywords:** Karst system, PAHs, seepage water, passive sampler, epikarst, flow paths, high-flow events

## 6.1 Introduction

Particles are an environmental key parameter for the overall understanding of the fate and transport of PAHs. However, little investigation has been done concerning the content of PAHs in water, especially in uncontaminated sites. Instead, all other compartments have been excessively investigated, e.g. sediments (FERNANDEZ et al., 2000; JIANG et al., 1998; SIMCIK et al., 1996), soils (BIXIONG et al., 2006; DALLA VALLE et al., 2005), plants (HOWSAM et al., 2001; MÜLLER et al., 2001; PICCARDO et al., 2005), atmospheric deposition (GIGLIOTTI et al., 2005; GOCHT et al., 2007) and air (HALSALL et al., 1997; OLLIVON et al., 2002). Only a few publications could be found which focus on "clean" waters; most of them deal with surface water (FERNÁNDEZ et al., 2005; OLIVELLA, 2006; VILANOVA et al., 2001).

PAHs can exist dissolved and adsorbed onto suspended particulate matter in water. However, water has a low sorption capacity for PAHs and therefore they prefer to sorb on sediments and organic matter due to their higher partitioning coefficient $K_d$. An interaction of a contaminant with the mobile source to the solid phase results in increased contaminant mobility (KÖGEL-KNABNER and TOTSCHE, 1998).

The most important input factor for PAHs into a specific area is the atmospheric deposition, especially the wet deposition (all kinds of precipitation) (MATZNER, 1984). This way of input is diffuse, ubiquitous, and more or less constant in an area with the same conditions. Snow can also act as reservoir for contaminants; it accumulates PAHs during winter and with the snowmelt they get suddenly released and can reach the groundwater (BLAIS et al., 2001; HERBERT et al., 2004). Furthermore, snow can scavenge both particulate and gaseous phase SVOCs (FRANZ and EISENREICH, 1998). During the snowmelts the flow velocity increases due to increased infiltration and it is possible to mobilise and transport water and particles. The latter can be important pollutant carriers due to their large surface-to-volume ratio and their chemical properties. It was demonstrated that colloids can act as carriers for contaminants (ATTEIA and KOZEL, 1997; ATTEIA et al., 1998). However, the transport of particles in karstic media is a complex process implying deposition and release phenomena. There are two potential origins: (i) the direct transfer of particles from the soils to the outlet of the karstic system (allochthonous origin) and (ii) the resuspension of previously deposited sediments inside the karst (sub-autochthonous origin) (DUSSART-BAPTISTA et al., 2003).

Another input source into the aquifer could be also point sources like vehicle washing (RULE et al., 2006). According to WILLIAMS (1993) due to their geological, morphological and hydrological features karst landscapes are highly vulnerable to a variety of degradation and pollution processes.

Normally, expensive devices have to be built up if the seepage water is studied, e.g. lysimeters. This is because the unsaturated zone is hardly accessible, but in a karst area it is possible to go access it through caves. HÖTZL (1999) wrote that the seepage water can reach the groundwater very fast along fissures and joints to be subsequently transported very quickly over large distances. For example, VILLINGER and UFRECHT (1989) reported for the study area (Blautopf Catchment, Southern Germany) flow velocities up to 350 m $h^{-1}$. Normal groundwater velocities in a porous aquifer are around 1 m $d^{-1}$. Furthermore, karst water is used as drinking water for 25 % of the world`s population (DREW & HÖTZL, 1999; FORD & WILLIAMS, 1989) and a particular protection should be considered seeing that drinking water is becoming a scarce resource. In the German Drinking Water Ordinance from 2001 the limit for BaP is given with 10 ng $L^{-1}$ and the sum out of BbF, BkF, BghiP and Indo should not exceed 100 ng $L^{-1}$ (TRINKWASSERVERORDNUNG, 2001).

Karstification is a continuous process, caused by natural and/or anthropogenic interactions, so that even the most precise models and/or approaches are only temporally valid (FORD and WILLIAMS, 1989; WHITE, 1988).

In a previous study GOCHT (2005) explored a catchment in the Black Forest and showed that almost all PAHs were accumulated in the soils and did not get released. We decided to study a karst area because of its higher vulnerability. Furthermore, there we have the possibility to go into the vadose zone by using caves and check the seepage water directly, without any disturbances. To sample the seepage water, passive sampler devices were installed in four different caves. This study is part of a mass balance in this area.

## 6.2 Materials and Methods

### 6.2.1 Sampling Sites

The studied area was located in Southern Germany on the plateau of the "Schwäbische Alb". The location of the sampling points is shown in Fig. 2.1. Four different caves were chosen for this investigation: "Hawaii-Schacht" (HWS, 9°40'52'' E, 48°27'29'' N), "Laichinger Tiefenhöhle" (LTH, 9°41'36'' E, 48°28'43'' N), "Sontheimer Höhle" (SH, 9°41'02'' E, 48°25'52'' N) and "Steingau Höhle" (StH). The coordinates from StH are not given in the interest of cave protection. These four caves are situated in the catchment area of the Blautopf which is the second largest karst spring in Germany. The catchment extends over four maps (GK 25, scale 1:25000): 7423 (Wiesensteig), 7424 (Deggingen), 7523 (Bad Urach) and 7524 (Blaubeuren). It has a size of 165 km$^2$, which consists mostly of agricultural land. The depth of the sampling locations beneath the surface was acquired with the help of the cave and the topographical maps. The depths were -8 m (HWS), -33 m (LTH), -45 m (SH) and -6 m (StH).

The karst aquifer is built up by the Upper Jurassic limestones from Oxford 2 (ox 2) up to Tithon (tiL) (GWINNER, 1989), whereas the unsaturated zone shows a thickness of about 100-150 m.

An average rain deposit for the Blautopf Catchment was calculated by POSTIGO REBELLO, (2006) and given at 1057 mm. The groundwater recharge in the Blautopf Catchment is about 500 mm a$^{-1}$ (ARMBRUSTER, 2002).

### 6.2.2 Time Integrated Passive Sampler (TIpS)

To investigate the concentrations of PAHs in the caves, passive samplers for atmospheric deposition (GOCHT and GRATHWOHL, 2004; MARTIN and GRATHWOHL, 2002) were used and modified (Fig. 6.1). Same sized cartridges with the same amount of adsorber material Amberlite™ IRA-743 were installed. Above the cartridge, there was a funnel made of stainless steel and 23 cm in diameter. Its function was to catch water from several places where seepage water dripped. At the beginning it was assumed that the concentration of PAHs in the seepage water is in the range of 0-10 ng L$^{-1}$. To exceed the detection limit an amount of more than 50 L should have flowed through the cartridge to get clear and reliable values. The water volume which passed the adsorber material was determined via a bucket at the runout (with volumes between 12 and 20 L). The latter was closed with a lid, so no additional water could drip in.

The bucket had to be emptied every 1-2 weeks, dependent on the amount of seepage water. During winter it was necessary to empty it every week, especially in the LTH, and in summer it was sufficient to go there every 2-3 weeks (in general). In the SH and StH, the amount of water was very little, so it was sufficient to go there less often. At all four locations two passive samplers were installed. One was installed below a fast and the other below a slow dripping place. At the latter the exact water volume could be determined, whereas the fast one had very often overflown. Additionally, this arrangement allowed us to see if there were different effects along slow and heavy flow paths through fissures.

The sampling periods were from 30.4.2004-30.4.2006 for HWS, 9.7.2004-30.4.2006 for StH, 19.3.2004-30.3.2006 for SH and 30.4.2004-19.7.2006 for LTH. In these periods the quantum of samples varied strongly; for example, in StH only three samples in almost two years could be taken due to the little seepage water. However, this cave was interesting, because it was situated next to a larger highway and it did not have any soil cover. Above the HWS there was a concrete slab with a size of 4 x 2 m, but most of the surface water ran down the entry shaft and did not pass the soil cover/buffer. The passive sampler for atmospheric deposition GH SH, GH HWS and SL LTH I + II were situated directly above the caves with the same name, so the direct PAHs input was known (please refer to Chap. 3).

The cartridges were changed when at least 50 L or more water were collected. After the removal of the residual water they were closed very tightly and well wrapped for the transport. The funnels were cleaned with acetone soaked glass wool, which was also analysed in the lab. This cleaning procedure was efficient to eliminate the PAHs, as well as particles from the funnel. Sinter formed on the funnels could not be eliminated. The latter should not affect the fate of the PAHs on their way to the cartridge. All sampling periods and detailed results can be found in the appendix C.

From 11.11.2005 until 19.7.2006 an additional passive gaseous phase sampler was installed in LTH. The same kind of cartridge was used, but it was placed at a “dry” place in the nearby environment of the other samplers for the seepage water. It was made sure that no seepage water could enter the cartridge. But due to the high air humidity (> 95 %) the cartridge was always moist.

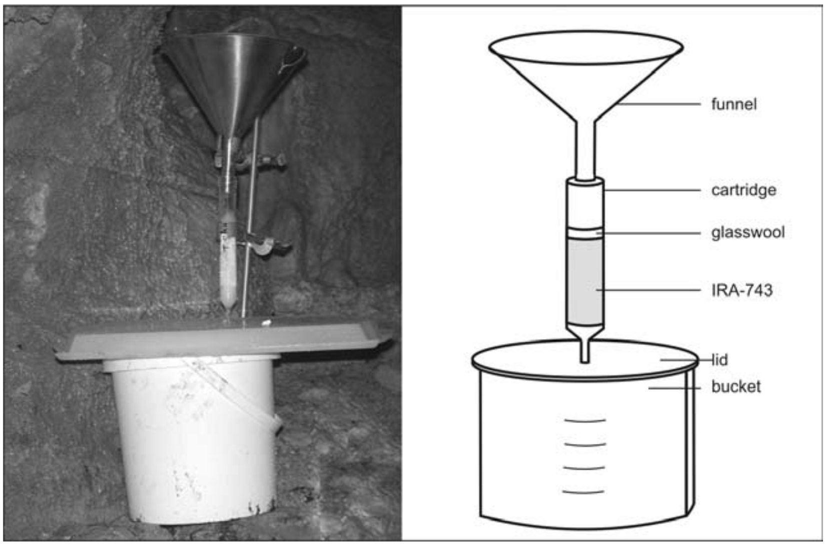

**FIGURE 6.1:** Assembly of the seepage water sampler in the cave (HWS).

For each sampling period a blank was carried along. The concentration in the seepage water $C_w$ was calculated based on the mass analysed in the adsorber material and divided by the volume of water collected in the bucket. The blank was handled the same way, but for calculation an average water volume of both time integrated passive samplers (TIpS) was used.

### 6.2.3 Water Samples

From March 2005 to 2006 additional water samples were taken in three of the caves. It was not possible to take water samples in StH, because the drip places were very rare. One or two litre bottles with a funnel made of stainless steel were disposed near the TIpS. It was not possible to sample at the same dripping place. Every time the buckets from the TIpS were emptied, the bottles were also changed. A disadvantage of this sampling method was that the bottles overflown almost every sampling period. This means the exact water volume could not be specified. Particularly for particles it would have been important to know the exact volume, because they could settle down and thus increase the content of PAHs, whereas the seepage water would flow out. Larger containers could not have been used, because transport of the containers in the narrow shafts, which required the use of ladders, would have been too difficult.

The liquid-liquid-extraction, analysis, clean-up and measurement of the samples (TIpS and water) were described elsewhere (Chap. 3).

### 6.2.4 Water Chemistry

The water chemistry parameters were measured with a multi-parameter instrument Multi 340i from WTW (Weilheim, Germany) at all four locations. With this instrument the following parameters could be measured: temperature and pH-value (SenTix® 41), oxygen (CellOx® 325), conductivity (TetraCon® 325) and redox potential (SenTix® ORP). All electrodes and sensors were calibrated on a regular basis to achieve a high quality measurement. They were employed directly in the buckets of the TIpS. In the LTH an additional bucket was used which sampled “fresh” seepage water to have a comparison in the case that the adsorber material influenced the water chemistry.

Additionally, the DOC was measured. Samples for this investigation were taken in HWS, LTH and in SH. The DOC measurement is explained in Chap. 5. The water for these analyses was taken from the water samples bottles (Chap. 1).

## 6.3 Results and Discussion

### 6.3.1 Time Integrated Passive Sampler (TIpS)

The concentrations for PAHs in the TIpS did not vary a lot; the values for HWS ranged between 2-846 ng $L^{-1}$ [blank: 1-27 ng $L^{-1}$], for LTH between 2-371 ng $L^{-1}$ [blank: n.d.], for SH between 3-9 ng $L^{-1}$ [blank: n.d.] and for StH between 6-46 ng $L^{-1}$ [blank < 3 ng $L^{-1}$]. The higher concentrations were always found in the sampler, which was located under the less and slower dripping place of seepage water. This could be due to a dilution effect, because the consideration of the larger amount of water eliminates the higher concentrations, although the adsorber material accumulated the PAHs. Lab experiments showed that the contact time with the adsorber material was sufficient for equilibrium even at fast flow rates (MARTIN, 2000; RING, 2006). Altogether drip rates did not remain constant during the monitoring, instead changing with the annual seasons. In summer the rates were lower due to less precipitation and higher evaporation on the surface. During winter and especially in spring (snowmelt) they were highest.

The distribution patterns for all four caves looked very similar. The five most prevalent PAHs are shown in Table 6.1. It is clearly visible that the LMW-PAHs (Phe), the intermediates with Fth, and Py as well as the HMW-PAHs via BbF, BaA and Indo are represented. This indicates that the main two different transport processes are involved: dissolved and particulate transport.

**TABLE 6.1:** The five most common PAHs in the different locations (HWS; LTH; SH and StH) and the average of all four.

| **Location** | **1. [%]** | **2. [%]** | **3. [%]** | **4. [%]** | **5. [%]** |
|---|---|---|---|---|---|
| HWS | Phe (20) | Fth (13) | Py (10) | BbF (8) | Indo (6) |
| LTH | Fth (16) | Py (12) | Phe (11) | BbF (9) | BaA (8) |
| SH | Phe (24) | Fth (10) | Py (9) | Indo (8) | BbF (7) |
| StH | Fth (12) | Phe (11) | BbF (11) | Indo (10) | Py (9) |
| *average* | *Phe (16)* | *Fth (13)* | *Py (10)* | *BbF (9)* | *Indo (7)* |

The background pattern of the blanks differed from the samples in all cases, although the concentrations in the samples were low. In Fig. 6.2 there are two locations presented for which a comparison of the blank with the samples is given. The blank always showed a high Phe appearance and a higher content of PAHs with less than 4 rings. The HMW-PAHs are not represented in the blanks. On the other hand the samples always showed a distribution pattern in which the heavier PAHs dominated, even if the concentrations were low. This shows that in all samples a transport or accumulation of PAHs occurred. A background contamination of the samples can thus be neglected.

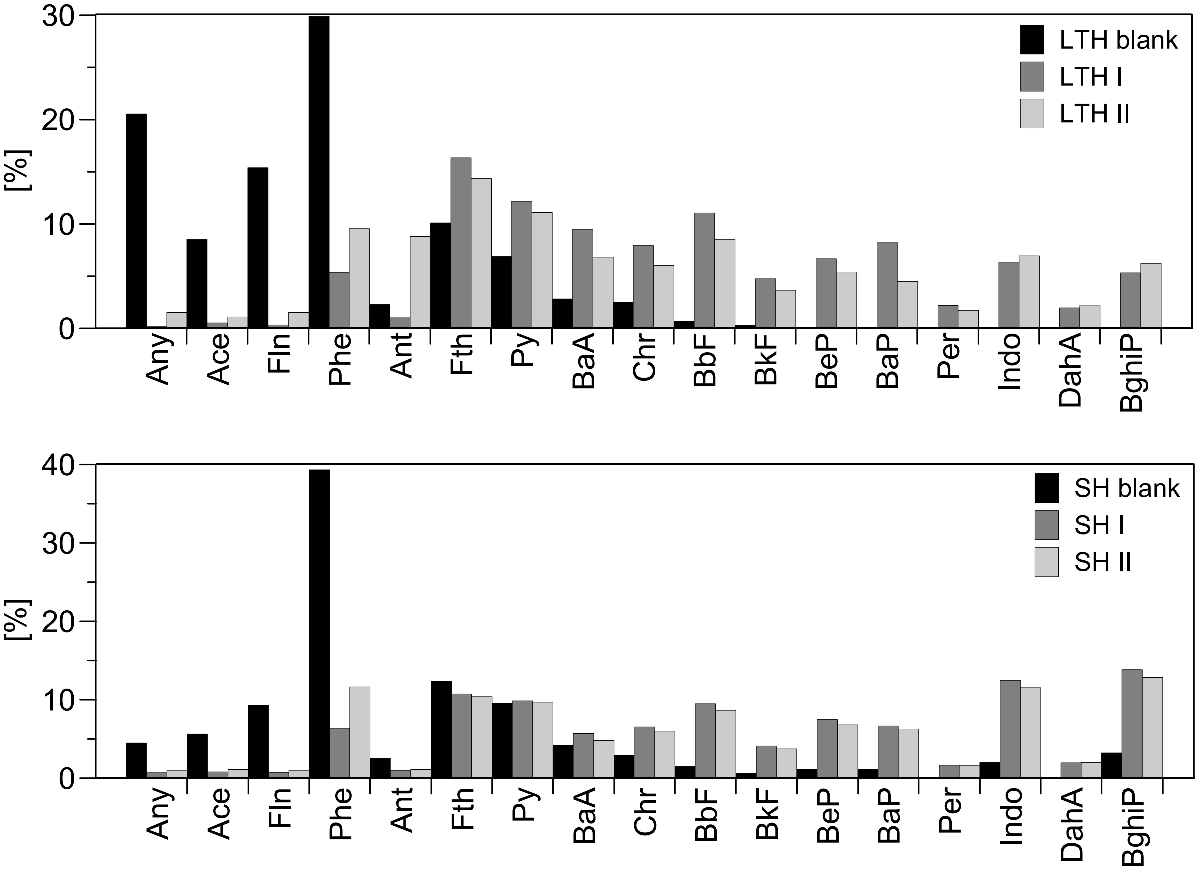

**FIGURE 6.2:** The upper graph shows the comparison between samples and blank in the cave of Laichingen, whereas the concentrations [ng $L^{-1}$] were: LTH I: 371 LTH II: 5, blank: n.d.. The lower graph shows the same, but for the cave of Sontheim: SH I: 9, SH II 3, blank: n.d. Note the different scales.

#### 6.3.1.1 Particle Transport and Calcite-Precipitation

A large problem was that during high flow events many particles appeared in the cave and thus blocked the cartridges. Particularly small particles (clay and silt) with a larger silt fraction were trapped in the cartridges. This meant they had to be changed within days, to lose no information from important periods (snowmelts, heavy rain events). Such events could be foreseen with the weather forecast. Another problem was that especially in the LTH the adsorber material sintered very fast and the IRA was cemented to one block. It is not clear if the IRA still could adsorb the PAHs from the water when the surface was surrounded by calcite. In the laboratory the liquid-liquid extraction of the adsorber material was first treated with hydrochloric acid (HCl, 16 %) to separate the grains to create a larger surface for extraction. Afterwards they were treated the same way as the others. These samples were marked with $^{\#HCL}$ and an additional blank value is given for the analysis of HCl. This was done to ensure that no PAHs were derived from the HCl.

In most of the cases the ratio LMW:HMW-PAHs indicated that the main part of the contamination was delivered via particulate transport, because the HMW-PAHs dominated often.

#### 6.3.1.2 Calculation of Concentrations in the Seepage Water

The sorption of hydrophobic organic compounds in soils is controlled by the type of organic matter (BURKHARD, 2000; GRATHWOHL, 2000; KLEINEIDAM et al., 2002). Therefore the $K_d$ value can be estimated with the organic carbon content $f_{oc}$ [-] and the organic carbon normalised partitioning coefficient $K_{ow}$ [$L^3$ $M^{-1}$] between octanol and water:

$$K_d = K_{oc} \cdot f_{oc}\ ,\ K_d = \frac{C_s}{C_w} \qquad [6.1]$$

It is possible to estimate the partitioning coefficient $K_{oc}$ with the following equation, if the $K_{ow}$ [$L^3$ $L^{-3}$] or the solubility S [mol $L^{-3}$] is known:

$$\log K_{oc} = \left(a \cdot \log K_{ow} - b\right) f_{oc} \qquad [6.2]$$

where $C_w$ is the concentration in water, $C_s$ the concentration in the solids, a and b are empirical constants. KARICKHOFF et al. (1979) applied 1.0 for a and 0.21 for b and used these constants in calculation. The soil BP LTH Sp2 is located above the cave of "Laichingen", so this soil was taken for the comparison between the calculated and measured concentration.

In the range of the intermediate and the LMW-PAHs there is a good agreement considering the distribution pattern of the measured and the calculated results (Fig. 6.3). The HMW-PAHs are below detection limit because of their very low solubility in water. However, the calculated $C_w$ from the top soil is 130 ng $L^{-1}$ (linear) and the non-linear one is even lower (0.7 ng $L^{-1}$). The concentration range of the TIpS was 2-371 ng $L^{-1}$, this shows that the calculated and measured results are similar.

The distribution patterns indicate that PAHs are transported in association with particles. Concentrations measured in the seepage water reflect the distribution pattern of the soils (Chap. 4). This also gives evidence of a particulate transport.

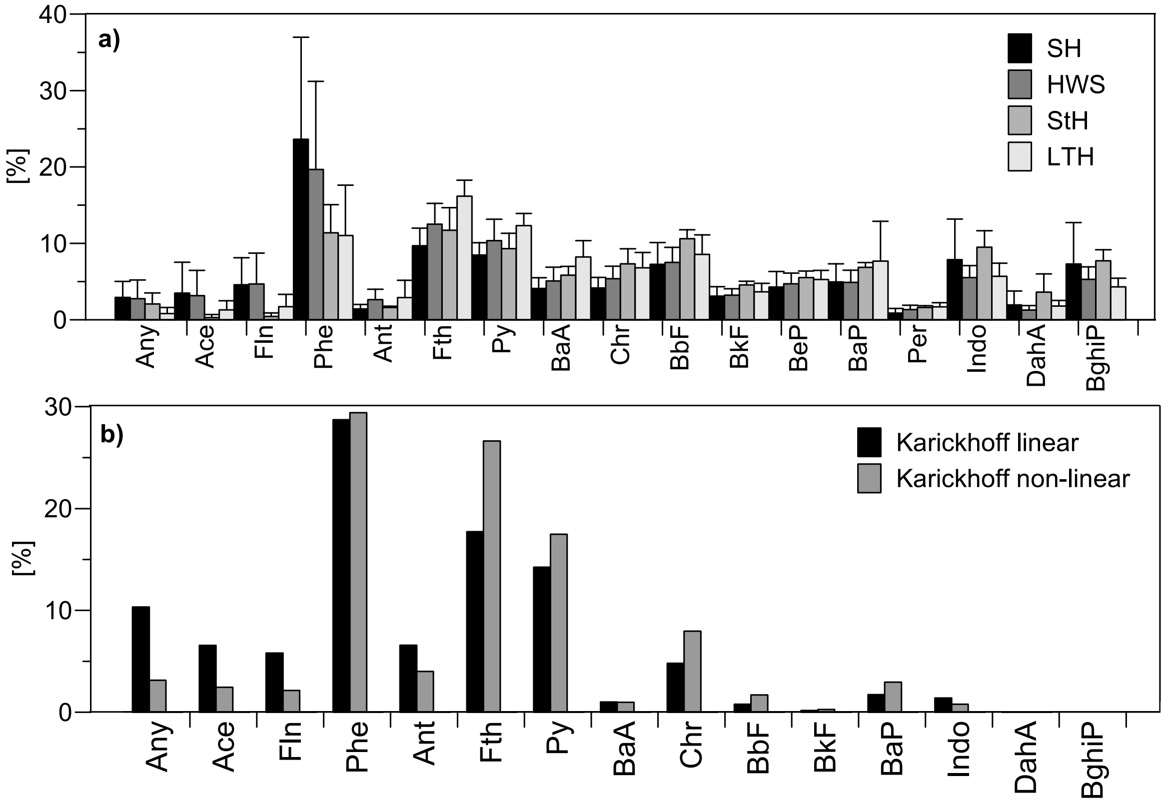

**FIGURE 6.3:** Distribution pattern of the measured seepage water in the caves (a) and the calculated concentrations in the seepage water (b), used soil BP LTH Sp2.

### 6.3.2 Water Samples

The water samples showed wider ranges concerning the PAHs: HWS ≤ 970 ng $L^{-1}$, LTH ≤ 34703 ng $L^{-1}$ and SH ≤ 51 ng $L^{-1}$. These values cannot be considered as absolute values, because the exact volume of water was not always known. However, they give an indication of the content of PAHs in the seepage water. Furthermore, they showed larger changes over time, which got partially lost with the use of the TIpS, because of the longer sampling period. The percentage for the average distribution patterns for the three locations can be seen in Table 6.2. The water samples showed similar results as the TIpS. Indeed the only HMW-PAHs was BbF, which indicates a less accentuated particulate transport than in the TIpS.

**TABLE 6.2:** Average distribution percentage of the water samples in different caves.

| **Location** | **1. [%]** | **2. [%]** | **3. [%]** | **4. [%]** | **5. [%]** |
|---|---|---|---|---|---|
| HWS | Fth (13) | Ant (13) | Py (13) | Phe (10) | BbF (8) |
| LTH | Fth (18) | Phe (15) | Py (13) | BbF (9) | BaA (8) |
| SH | Phe (27) | Fth (14) | Py (11) | BbF (7) | BaA (6) |
| Average of all caves | Phe (17) | Fth (15) | Py (11) | BbF (8) | BaA (7) |

### 6.3.3 Comparison of the Two Different Methods

To get an idea of the significance of the new TIpS for seepage water, it was necessary to compare them with the water samples. A similarity or contrast can give evidence of the reliability of the new method. In the following sections the results for the different caves are given.

#### 6.3.3.1 "Hawaii-Schacht" (HWS)

The water and TIpS samples from the HWS locations did agree in concentration of PAHs in almost all events. This can be seen in Fig. 6.4, where a comparison of the two methods is presented.

All events with exception of the second (Fig. 6.4) can be found in both sampling methods. This shows that the TIpS can display events if the sampling period was not too long. However, the sewage sludge inflow could not be seen in all samplers at the same time, due to the different pathways of the contaminated water.

In January 2005 potential influence of sewage sludge was observed indicated by scent and high organic content (DOC). There, only HWS I was contaminated with a concentration of 970 ng $L^{-1}$. To determine the concentration of PAHs for this event two extra water samples were taken, whereas the preparation in the laboratory was not easy. The detected values were 225 and 146 ng $L^{-1}$. These results were not as high as in the TIpS, but the water was just the rest which remained in a depression of the cave. The fragmentation of the distribution patterns into snowmelt, sewage sludge and others (normal infiltration) resulted in different percentages (Fig. 6.5). The pattern for “the others” is dominated by the LMW-PAHs (Phe, Ant). It can be interpreted that along “normal infiltration” (= slow) there was enough time to adsorb the LMW-PAHs from the soils, especially Phe and Ant. Hence, the snowmelt and sewage sludge showed higher percentage of the heavier PAHs. Since blanks did not show any of the HMW-PAHs, background contaminations can be excluded. Even during non-events there is also a clear trend towards a particle associated transport of PAHs.

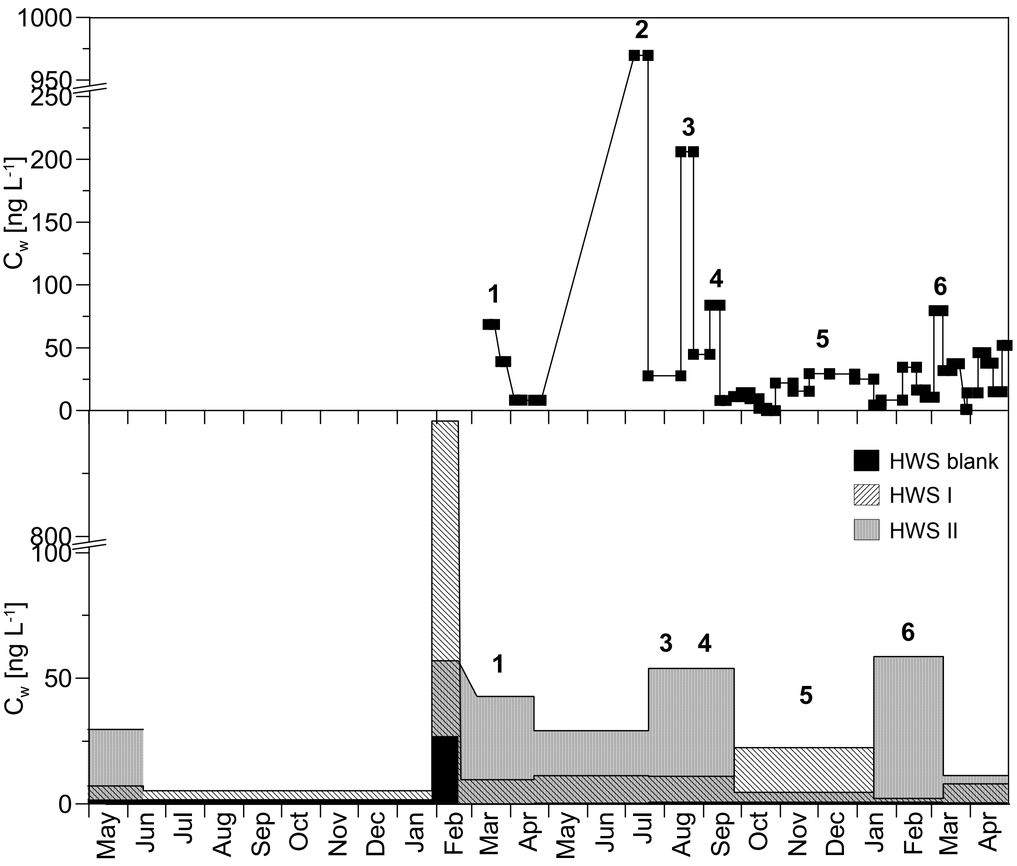

**FIGURE 6.4:** Comparison of the two different sampling methods in the Hawaii-Schacht. Upper graph shows the water samples and the lower the time integrated passive sampler. Number indicate different events: 1. during a snowmelt event, 2. inflow of sewage sludge, 3. unknown, 4. inflow of sewage sludge, 5. base flow and 6. during a snowmelt event.

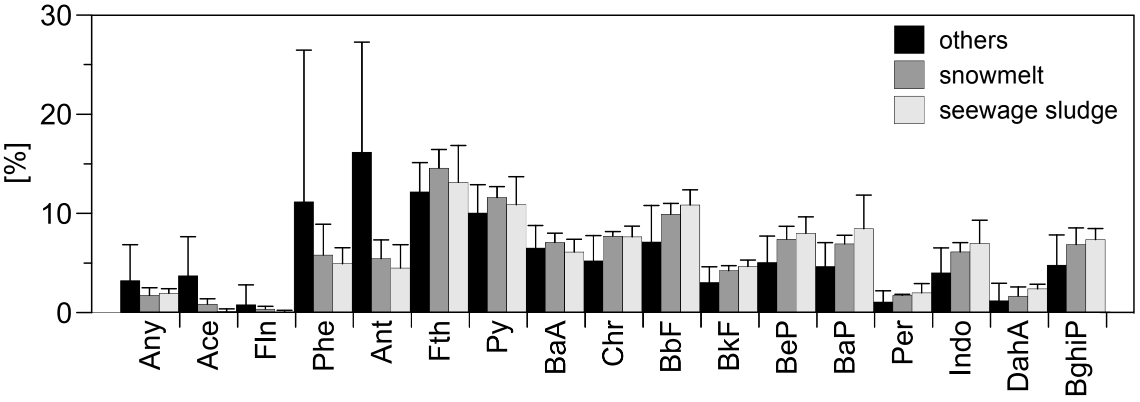

**FIGURE 6.5:** Distribution pattern of different events in the "Hawaii-Schacht", others imply all time periods, in which nothing special happened, only normal infiltration.

### 6.3.3.2 "Laichinger Tiefenhöhle" (LTH)

A good correlation was also found between the events in LTH for the two different methods. There were two events, both snowmelts in March (2005 and 2006). They could be seen in the water samples as well as in the TIpS. During the same period as in HWS (in fall and winter) the concentrations were also low. During the snowmelt in 2005 the BaP concentration exceeded clearly the German limit for potable water, reaching 35 ng $L^{-1}$. This shows that there is an exposure to the input of PAHs during lateral heavy precipitation events, especially snowmelts in karst areas. In HWS there was also one transgression of the protection limit with 48 ng $L^{-1}$ during the inflow of sewage sludge.

#### 6.3.3.3 "Steingau Höhle" (StH)

The results from StH had the disadvantage of long sampling periods. Thus, the events could not be seen as clearly as in HWS and LTH, because the events with higher PAHs concentrations were diluted by the normal (= very low) concentrations. However, it was possible to see the snowmelt event from 2005 in the sampler StH I. On the other hand, in the second sampler the concentration was high at the beginning of the sampling period and decreased continuously. It could not be clarified why this happened. The distribution pattern for StH showed more or less the same as the others did, although there was no soil cover above the cave. This means that the particles which are responsible for the PAHs input come at least partially direct from the precipitation.

#### 6.3.3.4 "Sontheimer Höhle" (SH)

In SH it was not possible to find any correlations between the different methods. The main problem in this cave, as well as in the "Steingau Höhle", was that the sampling periods were too long to single out the events. This was caused by the overall low concentrations in the samples and the very rare seepage water. The small concentrations measured could also be referred to a particle bound transport.

### 6.3.4 General Results

It is known that the amount of particles increases during high flow events, but sources of the particles may be allochthonous or autochthonous. Relevant transport and sorption processes take place in the soil and epikarst zone (subcutaneous zone). According to SAUTER (1995) and WILLIAMS (1983) the water in the epikarst flows at first lateral till it hits an open pit to supply the groundwater. An overland flow in a karst area can be neglected, because all the precipitation water infiltrates very fast. This indicates that the water has more time to adsorb the PAHs onto the soils and the epikarst matrix. However, it is possible that the rain water passes these compartments without any PAHs being lost and thus reaches the caves with the whole load of PAHs. SPÖTL (2004) talks about broad storage and mixing processes in the karst system, which means that the infiltrating water needs a long time till it reaches the cave.

During snowmelt events a lot of water infiltrates the soil. Older water gets pushed away (piston flow effect) and finally enters the cave. Additionally, preferential flow paths and larger conduits allow new water to enter the caves quickly and this gets mixed with the older water. FRANZ & EISENREICH (1998) realised that snow can act as an efficient scavenger of vapour and particulate atmospheric pollutants. This can be a reason why the snowmelts showed larger influence on the concentration than the thunderstorms in summer did. Additionally, the amount of infiltrating water was also higher during snowmelt events.

Groundwater flow paths can be highly irregular because of the heterogeneous distribution of fractures in most natural systems (COOK et al., 2005). This fact was given in the studied area, because the drip places showed different connections to the surface; some were connected with good permeable conduits/fissures while others were poorly connected with lower amount of seepage water, but higher concentrations of PAHs.

Subsurface contaminant migration is controlled by convection (advection) and dispersion, but in low-permeability rocks, diffusion may become a dominant transport mechanism (POLAK et al., 2002). In fractured porous media the solute transport is characterised by rapid advection through the fractures, with diffusive exchange between solute in the fractures and in the relatively immobile water in the matrix (COOK et al., 2005). This would mean that the slow seepage water sorbed the PAHs from the porous rock matrix and transported it.

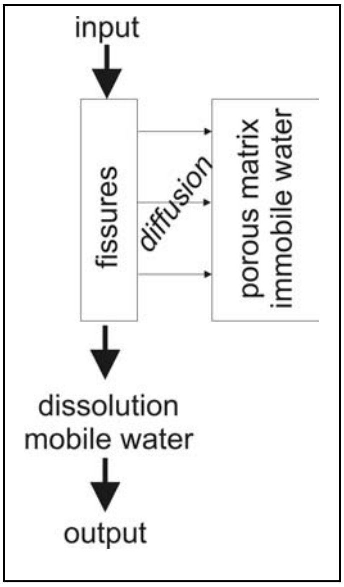

**FIGURE 6.6:** Schematical sorption conception of the procedures in the limestone along fissures.

SEILER et al. (1989) compared dispersivities from a karst area on the “Fränkische Alb“ with some in porous gravels in southern Germany. They concluded that dispersivities in the karst were lower than those in porous media.

It should be considered that a main part of the transport in the vadose zone takes place in the limestone. The concentration of PAHs of the limestone should be low, because of the low sorption capacity. Some fissures are refilled by clays and loamy sediments which do not have a large sorption capacity and which date back to the lower and middle Oligocene (DEHM, 1970; DEHM, 1978; UFRECHT, 1983) and thus should also not have a high content of PAHs, unless later pollutions came along, like oil or other highly polluted seepage water infiltration.

Since the matrix permeability of the rocks is low, fractures and joints provide main pathways for rapid water flow and solute migration, enabling the contamination of large volumes of rock (POLAK et al., 2002).

There are still some open questions which should be clarified in further research. It is not known how long the infiltrating water needs to pass the soil and epikarst zone to reach the cave. Therefore some investigations have already been done with stable isotope applications, but no significant result considering the transit time could be asserted (Chap. 9). Furthermore, the main processes in the above mentioned zones are not clear, as well as the role of the rock matrix. What happens with the PAHs, especially the particulate ones, when they enter the vadose zone?

To apply the TIpS in further studies some important rules should be considered:

1. At least two sampler locations in one cave with different dripping rates (best triplicate).
2. Two or more locations in the cave with different depths of coverage.
3. The dripping rate should not be too low, 50 L in maximal 2 months, especially in summer.
4. Easy access, even though there is bad weather.

### 6.3.5 Dissolved Organic Carbon in the Seepage Water

The DOC was measured in the period from March 2005 till August 2006. In LTH it varied between 0.9 and 1.8 mg $L^{-1}$, including all three different sampling sites (TK, VH and NS). The exact location of these sites in the cave is given in Fig. 8.2. In the other caves it was in the range of 0.9-2.6 mg $L^{-1}$ (SH) and 1.8-3.2 mg $L^{-1}$ (HWS). Fig. 6.7. shows all three graphs.

The results from the different caves showed different trends over the sampling period. In SH the DOC increased continuously from the beginning to the end, so it reached the highest values in March 2006 (end of sampling at this location). The trend in HWS increased from March till October and decreased afterwards.

In the cave of Laichingen the DOC did not show any trend, but rather fluctuated over the whole sampling period. At the end of February the location TK was abandoned and two other drip places were used for sampling instead (NS and VH). This was done because the TK water was totally used for the analysis of PAHs. However, they showed a clear decrease in summer. This was only insignificant in August and September in the summer before.

It was expected that the DOC concentration would be higher in summer during the period of high biological activity. But this was not given in the investigated caves. TOTH (1998) measured the DOC content with the help of fluorescence in a cave in southern Indiana and she observed highest concentrations during springtime and lowest in summer and fall. This result would fit with the finding of the LTH. EMBLANCH et al. (1998) found out that with longer residence times the mineralization of DOC into mineral carbon increases. That means that during high flow events the DOC should increase, because there is not enough time to mineralize. This also fits with the findings of this work, because during spring and winter time there is more seepage water than in summer. DOC is too low to influence the transport of

POPs. It behaves as solute and is well buffered in the soil and epikarst. Thus, it is not possible to use the DOC as tracer for residence time in caves, because the differences between the various seasons and events are too small.

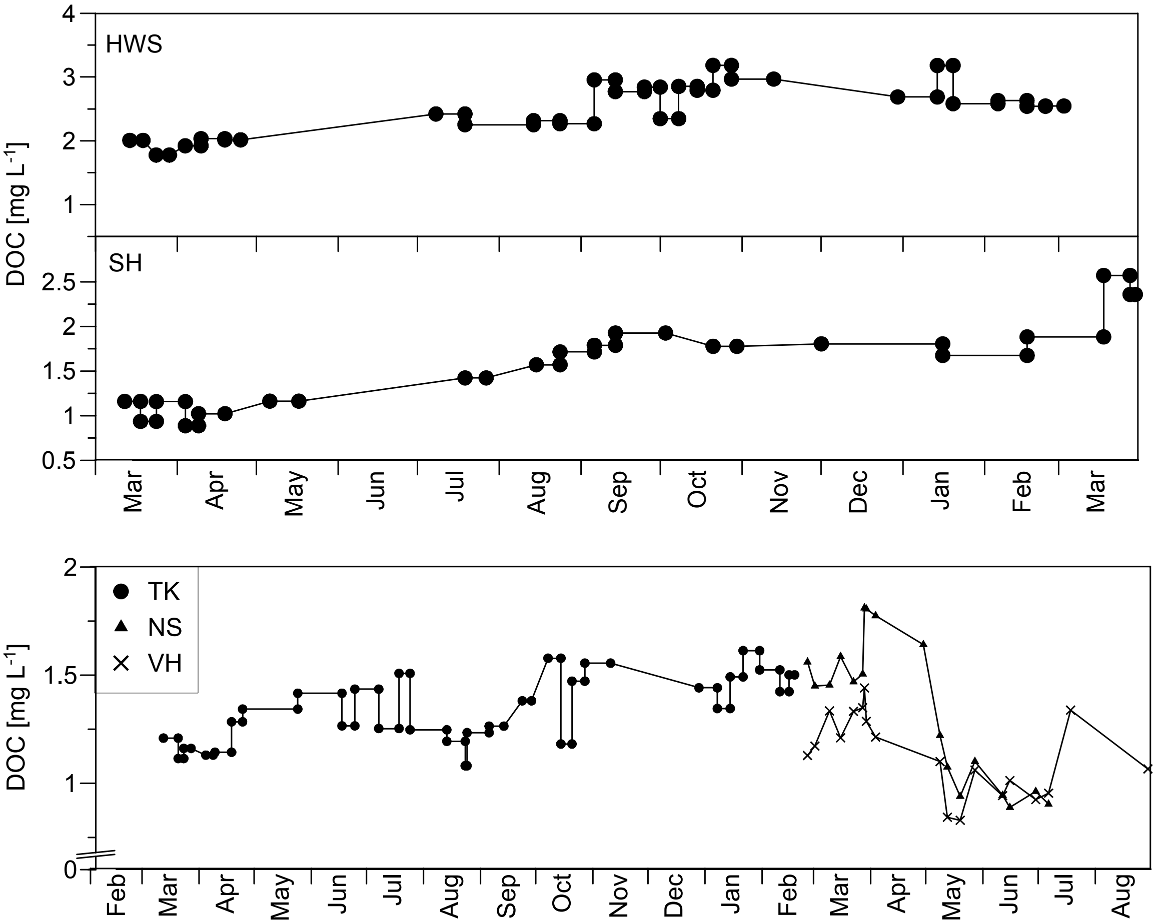

**FIGURE 6.7:** The upper graph shows the DOC content in HWS and SH. The lower one the DOC in LTH at three different sites: TK, NS and VH.

### 6.3.6 Water Chemistry

The water chemistry in the caves is mainly controlled by the rock-water interaction along the flow paths in the vadose zone. It depends on the transit time and the mixing processes. The values of all four locations is given in Table 6.3.

The behaviour of the parameters in the seepage water are described with the location LTH, because here the best results were obtained. The temperature showed a clearly seasonal cycle, higher temperatures in summer and lower ones in winter. Consistent with this graph is the one from the conductivity and within the redox potential this trend is slightly indicated. However, the redox potential is overlaid by larger fluctuations. The pH-value is contrary to the temperature. These results show a dependency of the conductivity, the redox potential and the pH-value on the temperature. This would mean with increasing temperature the dissociation of electrolytes in the aqueous phase also increases and thus the conductivity arises. The additional gauging station showed no deviation from the TIpS ones.

**TABLE 6.3:** Minimum and maximum values for the water parameters at the different locations.

| **Parameter** | **HWS** | | **LTH** | | **SH** | | **StH** | |
|---|---|---|---|---|---|---|---|---|
| | **I** | **II** | **I** | **II** | **I** | **II** | **I** | **II** |
| $O_2$ [mg $L^{-1}$] | 8.7-11.5 | 8.8-11.5 | 8.8-11.3 | 8.2-10.9 | 9.1-12.2 | 8.3-12.0 | 7.7-12.0 | 7.7-11.9 |
| pH | 7.1-8.1 | 7.1-8.1 | 7.0-8.3 | 6.2-8.0 | 6.9-8.7 | 7.0-8.7 | 6.9-8.4 | 7.0-8.3 |
| conductivity [µS $cm^{-1}$] | 440-604 | 150-782 | 346-620 | 364-692 | 212-666 | 236-1155 | 160-415 | 217-484 |
| T [°C] | 6.2-8.5 | 6.3-8.2 | 8.6-9.3 | 8.6-9.3 | 5.0-6.8 | 5.1-7.1 | 5.4-11.5 | 5.2-11.5 |
| redox potential [mV] | 136-293 | 138-288 | 136-275 | 138-295 | 153-284 | 146-334 | 129-294 | 133-308 |

Oxygen concentrations are fairly stable over time; only two outliers exist. These were caused by a defect of the instrument or the sensor. HECK & HILLER (1993) measured the same parameters in the LTH at different locations and they found that there were places in the cave that showed seasonal fluctuation and some that did not. This probably depends on the flow rate through the rock and the fissures. A high velocity means less contact time and thus lower sorption processes of contaminants. To investigate high flow events or the residence time of water continuous measurement of all parameters would be helpful. Additionally, the drip rate should also be determined, to have a clue of the beginning and ending of an event.

## 6.4 Summary

With the investigations of this study it is possible to monitor the transport processes in the seepage water of the Blautopf Catchment.

- The overall and most important result was that the German limit for drinking water was clearly exceeded in two caves. Normally, the concentrations of PAHs were very low, but during high discharge events, like snowmelts, they increased obviously (hundredfold).
- By means of the distribution patterns it was possible to show that transport processes mainly take place in association with particles. The dissolved percentage of PAHs is not important for transport processes in the study area.
- DOC was almost constant, even during high discharge events and did not influence transport of PAHs. The water parameters did not show any large variances, too. This also gives evidence of a particle bound transport, because the dissolved part in the water did not change during events.

These results confirm the assumption that most PAHs are stored in the soils. Export of PAHs via groundwater to the Blautopf Spring is very low.

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# CHAPTER 7

# PAHS IN THE GROUNDWATER OF A KARST SYSTEM IN THE BLAUTOPF SPRING, SOUTHERN GERMANY

**Abstract**

The "Schwäbische Alb" is one of the largest karst areas in Germany. The second largest karst spring is located in the Blautopf Spring (Blautopf), which shows a highly variable discharge ranging from 0.3 to 32 $m^3 s^{-1}$. The extension of the catchment area is about 165 $km^2$. This area is mainly used for agricultural purposes, so background pollution levels can be obtained.

In principal, karst aquifers have a high vulnerability for the input of contaminants because of their thin soil layer, many sinkholes, and other direct pathways to the groundwater. The objective of this study was to determine the output of polycyclic aromatic hydrocarbons (PAHs) in the groundwater. Concentrations of PAHs in the spring were monitored using a time-integrated sampler. Therefore, the pollutant fluxes could be fully measured in time and space, integrated over a one-year period. The highest concentrations (300 ng $L^{-1}$) were determined during a snowmelt event with an elevated suspended load in the spring. At that time the limit for benz(a)pyrene in drinking water was exceeded. The concentrations of PAHs in the groundwater correlate very well with the discharge and the turbidity of the spring. During normal discharge only very low concentrations were determined. During the high flow events the output of PAHs was dominated by particle facilitated transport.

**Keywords:** PAHs, time integrated monitoring, karst spring, groundwater, "Schwäbische Alb" (Swabian Alb), high flow event

## 7.1 Introduction

Previous research on water contamination within a karstic system has mainly focused on lakes and rivers (BARRA et al., 2005; FERNÁNDEZ et al., 2005; OLIVELLA, 2006) and not on groundwater. Presently, the main focus has turned its attention to contaminated karst sites and their remediation, as well as natural attenuation of contamination (FUCHS et al., 2006; GUSTAVSON and HARKIN, 2000; LANDMEYER et al., 1998; MUELLER et al., 1991; ROBINSON et al., 2006; ZAMFIRESCU and GRATHWOHL, 2001).

PAHs have a low water solubility and high partitioning coefficient towards organic matter (BARRA et al., 2005). In the water they occur as dissolved compounds as well as bound to suspended solids. The classical size classification is as follows: colloids $\leq 0.45$ µm < particles (HOFMANN et al., 2003). Colloids can act as carriers for contaminants (ATTEIA and KOZEL, 1997; ATTEIA et al., 1998). Furthermore, due to the large surface-to-volume ratio and chemical properties, they can possess a charge over a large surface area (ATTEIA and KOZEL, 1997; BUFFLE and LEPPARD, 1995). Due to these properties, it is concluded that a two-phase-model (dissolved and particle bound) should be considered for transport. According to SHEVENELL and MCCARTHY (2002) the potential role of colloids in contaminant transport is more significant in karst systems than in unconsolidated porous media or deep fractured sites. Due to this reason, particles in this investigation play an important part, particularly when considering heavy rain events, which cause an increase in discharge, which ultimately results in a mobilisation of colloids and particles.

BENES and STEINNES (1974) were among the first who established a passive sampling method to monitor the concentrations of dissolved inorganic compounds in surface waters. According to STUER-LAURIDSEN (2005) it is often desirable to expand the time window for sampling and increase the resolution by taking more samples, especially when the contaminant concentration changes. Nevertheless, he claims that this pseudo time-integrated water sampling (by hand) is both costly and cumbersome. This was also the main reason why a long-term and time-integrated monitoring system has been developed. PAHs have been chosen for this study due to the diffuse input from the atmosphere and their high ubiquitous concentrations. They can be used as ubiquitous environmental tracers. In general, karst aquifers have a high vulnerability for the input of contaminants because of a thin soil layer, many sinkholes, and other direct pathways to the groundwater. According to GABROVŠEK and

DREYBRODT (2001) hydraulic conductivities in a mature karst aquifer vary in the range from $10^{-10}$ up to $10^{-1}$ m $s^{-1}$.

Due to the ubiquitous distribution of PAHs and the high vulnerability of karst systems, the crucial part of this work was to find out which processes are relevant in transporting PAHs into the groundwater in karst aquifers. The spring was monitored over a period of about one and a half years and the developed sampling system has been tested. The total contaminant content and transport to the Blautopf Spring water depends on the release of PAHs from the soils due to the seepage water or from the direct precipitation input along vertical shafts.

## 7.2 Materials and Methods

### 7.2.1 Sampling Sites

The Blautopf is the second largest karst spring in Germany. The average discharge has been recorded at 2400 L $s^{-1}$, with the maximum level recorded at 32500 L $s^{-1}$. Almost all rainwater that infiltrates in the catchment (165 $km^2$) discharges at the Blautopf, which is the main outlet of the system. There is only one small spring nearby (“Gerhauser Quelle”), which will be neglected in the following description because of its small discharge (HERRGESELL, 1992).

The Upper Jurassic of the "Schwäbische Alb" is a fissure and karst aquifer. A typical phenomenon of springs in such areas is an erratic discharge. Thus the Blautopf, which has big water height differences, shows a fast reaction to rain events. This behaviour indicates a strong karstification of the Kimmeridge and Tithon limestones (VILLINGER, 1987). In 2005, the Arbeitsgemeinschaft Blautopf (ARGE Blautopf) found large halls in the caves behind the Blautopf, confirming strong karstification (www.blautopf.org). At the moment there are more than 2660 caves known in the "Schwäbische Alb" (FRANK, Organiser of the cave register "Schwäbische Alb", pers. com.), which is the largest karst region in Germany. Around 50 caves are situated in the Blautopf Catchment itself.

The catchment size has been investigated by tracer tests. They came up with peak velocities up to 350 m $h^{-1}$ (VILLINGER and UFRECHT, 1989), whereas the average flow rate was around 100 m $h^{-1}$ (GROSCHOPF, 1957; VILLINGER and UFRECHT, 1989). The tracer tests do not consider the heterogeneous flow systems, which can be fast (conduits) or slow (fissures). In general, sinkholes were used as input spots and thus the soils were bypassed. Furthermore, this means that the conduits were more or less used as pathways, whereas normally the main infiltration passes through the fissures (SELG et al., 2006). Since there is an important storage area at the top of the vadose zone (KLIMCHOUK, 2004; SAUTER, 1992a), the epikarst (subcutaneous zone) should not be neglected. The void volume of the Upper Jurassic has been estimated to be between 1 and 4 % (SAUTER, 1992b; VILLINGER, 1977). The hydrology of the system is described elsewhere (VILLINGER, 1978).

The "Schwäbische Alb" lies in the temperate zone. The annual average temperature lies at 6.5 °C, as taken from data recorded between 1961-1990 (MÜLLER-WESTERMEIER et al., 1999). The precipitation in the Blautopf Catchment is higher in the northwestern part (1100 mm) and decreases towards the southeastern part (800 mm) (KELLER, 2003). This increase of precipitation is due to the higher elevation in the northwest and a surface declination to the southeast (BEHRINGER, 1988).

### 7.2.2 Time Integrated Sampler

For the measurement of PAHs in the groundwater from the Blautopf karst spring, a time integrated sampler (Fig. 7.1) was developed based on the design of the atmospheric deposition samplers (Chap. 3). Special extraction cartridges made of stainless steel filled with approximately 13 g of the adsorber material Amberlite™ IRA-743 were used. The adsorber is composed of macro porous polystyrene with a methyl glucamine functionality. The most important properties of this adsorber material are described elsewhere (MARTIN, 2000; PIEPENBRINK, 1998).

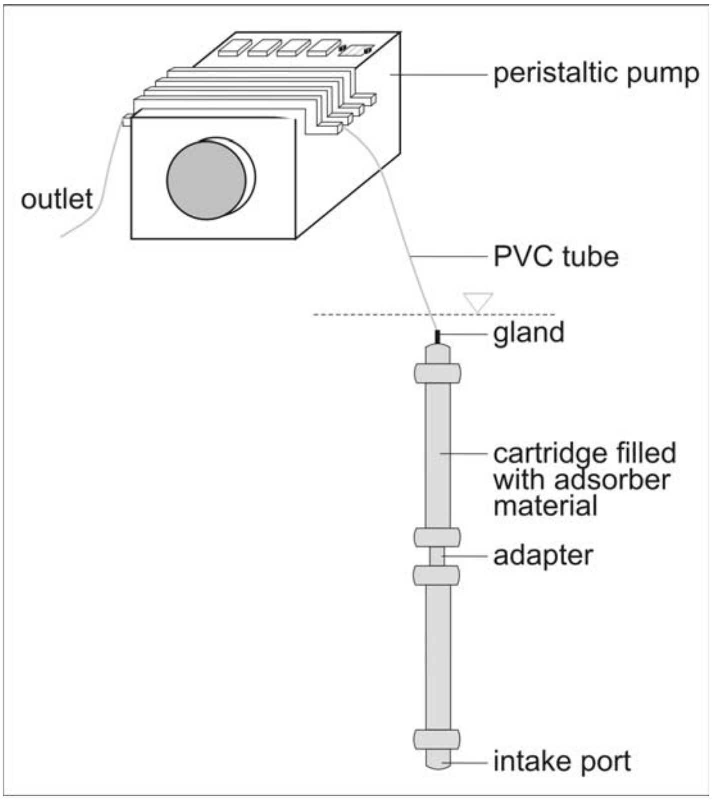

**FIGURE 7.1:** Assembly of the groundwater sampler in the Blautopf Spring.

Silica sand filters were built at both ends and in between the two cartridges, which were applied in a row. Additionally, three sieves with a mesh aperture of 0.75 mm (located at the ends and in between the two cartridges) were used. They were installed to restrain the filling and to block infiltration of unintended pollutants, such as algae, leaves, etc. from the spring water. One cartridge has a diameter of 1.3 cm and a length of 25 cm. Two of them combined are more than 50 cm long. Before they were deployed in the field, they had been wetted with Millipore water to facilitate wetting and the water flow in the field. Both cartridges were analysed separately. The first cartridge is termed the front cartridge (BT-v) and the second one the back cartridge (BT-h). If both cartridges are considered together, then it is named BT-g. The sampling period is added if necessary. At most, three cartridges were installed in the spring at one time. Due to their simultaneous presence in the spring, they are additionally named BT K1, BT K2, BT K3 and BT K4. The last of these was only used one time during the snowmelt in 2005.

Additionally, the cartridges were prepared at most two days before their application in the spring. Prior to their installation the PTFE tubing and the peristaltic pump (ISMATEC IPN) were positioned behind the cartridges to prevent any potential sorption. The tubes had a diameter of 6 mm. The length was kept as short as possible to avoid air bubbles in the system caused by possible leaking connections. The whole double cartridge composition was built entirely below the water surface. The height difference between the pump and the aperture of the cartridge was around 1.5 m. The cartridges hung vertical in the spring to ensure a constant stream flow towards and into it. This sampling system pumped the water of the spring continuously with average flow rates of 10 mL min$^{-1}$. To determine the flow rate, a measuring beaker was filled at the outflow and the time was recorded. This was repeated every 1-2 weeks. Variations in the flow rate, due to different reasons like tube volume changes, gave only approximate values of the volumetric flow rates. On the basis of the flow rates, the concentration in ng L$^{-1}$ per cartridge was calculated.

The tubes were changed about every second month. In summer they had become overgrown with algae and were additionally occupied by snails that had settled in the tubes. During winter the tubes froze as the temperature was close to -5 °C and below. When the tubes were completely frozen (which had happened several times) the total sampling system stopped and had to be restarted under better conditions.

All components made of plastic, metal, etc. had to be discarded because of the potential sorption processes and subsequent memory effects onto these materials. Glass, Teflon, and stainless steel were preferred.

One important disadvantage of this system is the need of electricity. This is why the monitoring system was not directly installed in the spring itself, but 80 m downstream in the river “Blau”. There is a pump station for water supply which has electricity and where nobody can damage the sampling system. Furthermore, the water level is kept constant because of the turbine driven by the river.

After a sampling period of 2-12 weeks, the cartridges were disconnected and closed tightly with aluminium foil on both sides. For this investigation, no special blanks were used because the second cartridge in a row could be used instead, since a breakthrough never occurred during sampling. The adsorber material was tested in the laboratory prior to use to ensure that there were no background concentrations. The sorption capacity of the IRA is rather high and the flow-through-velocity is moderately slow. Consequently the contact time is sufficient to adsorb all PAHs as shown by others (MARTIN, 2000; RING, 2006).

The analysis of the cartridges was performed the same way as the other IRA samples with liquid-liquid-extraction. This procedure is described elsewhere (Chap. 3).

### 7.2.3 Water Samples

To validate this new system, additional water samples (1 or 2 L) were collected. The water was taken from the Blautopf in a depth of 20 cm above the dam. There is always a flow of fresh water. The samples were stored at 4 °C in the dark before analysis. For extraction, an internal standard and 10 mL cyclohexane were added, shaken for one hour, and then the remaining space in the bottle was filled with Millipore water to allow sampling of the cyclohexane from the bottle neck. The water sample then sat for 24 hours, where afterwards the cyclohexane was extracted and minimized with the nitrogen stream to ~150 µL and measured at the GC-MS.

### 7.2.4 Particles

During the snowmelt of 2005, particles in the spring were collected. This was done with a vacuum Sartorius filtration apparatus and Whatman® glass microfibre filters with a pore size of 0.2 µm. This pore size was chosen because the colloidal particles (< 0.45 µm) were also of interest. The filtration apparatus, which was hanging directly in the spring, was connected to an extra pump (independent of the time integrated sampler), because stronger pumping was necessary due to fast clogging of the filters. Flow rates did not exceed 2 mL $min^{-1}$. The sampling time took one day and within this period around 1.0-1.5 L water were filtrated. The defined amount of particles per litre water is not crucial for the concentration of PAHs which is determined directly in µg $kg^{-1}$. The suspended load per litre was determined for different discharge events (which will be discussed later).

In the laboratory, the filters were stored and dried in an exsiccator. The particle amount was determined in grams using a precision balance with 4 decimal places. Afterwards, the particles were extracted using the accelerated solvent extractor (ASE). The particles had to be separated from the filter, because by the use of the ASE with its high temperatures of 150 °C the filter resolved and the sample was destroyed. The separation was performed by first rinsing the particles with acetone into a beaker. Following this procedure the filter was put in the acetone extract and into the ultrasonic device for 0.5-2 hours. Although it was not possible to get all the particles of the filter this problem was resolved by weighing the filter before and after the extraction procedure.

To extract this acetone-particle solution, the ASE cell (33 mL) was filled with two glass fibre filters first, followed by a silica sand (0.5 cm). This bedding procedure was repeated several times, until two-thirds of the cell was filled. Then the sample solution was added and the cell was filled up with silica sand and one last filter. The ASE extraction was performed the same way as described in Chap. 4.

### 7.2.5 Data Logger

In May 2004, the "ARGE Blautopf" installed a data logger in the Blautopf. This logger (Model 6920, YSI Incorporated, Ohio, USA) was fixed in the "Blauhöhle" at a depth of -31 m and around 70 m away from the entry of the underwater cave. It recorded water level, turbidity, conductivity and water temperature. More details are described by SELG et al. (2006).

## 7.3 Results and Discussion

### 7.3.1 Time Integrated Sampler

The concentrations of PAHs in the spring were at their highest at 56 ng $L^{-1}$, as taken from the average of all three cartridges (BT K1, BT K2 and BT K3). The long-time monitoring system could not accurately represent short term events with high concentrations (snowmelt, heavy rain events, etc.), because the concentrations were averaged over the whole sampling periods.

The highest concentration (56 ng $L^{-1}$) was detected during the snowmelt of 2006, which recorded a discharge above 25000 L $s^{-1}$ and an increased level of turbidity.

The mean distribution pattern of all three cartridges showed that Phe (15 %), Fth (12 %), Py (10 %), BghiP (9 %) and BbF (8 %) were the prevalent PAHs in the spring. This result agrees with the findings of the seepage water. Thus, the particle associated transport is important.

#### 7.3.1.1 Verifying the System

To exclude a breakthrough of contaminants, the values from the two cartridges constructed in a row were used. The PAHs measured in BT-v and BT-h showed that the majority stayed in the first cartridge (∑PAHs 85 %, n= 46) and only 15 % of the total was found in the second, even though around 1000 L were pumped through the whole system. The LMW-PAHs were found in BT-h with a higher percentage due to their higher water solubility (Fig. 7.2). HMW-PAHs were mostly found in the first cartridge because they were associated with the particles, which upon entering the system were filtered in the adsorber bed.

The adsorber material used in this sampling system was chosen for its good wettability, permeability, and stability with respect to swelling (MARTIN, 2000). Before the system was installed in the field, several tests had been made in the laboratory. First, glass wool was tested. Because the particles were held back by the glass wool, the entire cartridge was completely blocked. Silica sand was the more appropriate solution because then some particles could flow through and be dispensed in the rear part.

Laboratory column experiments showed that with a smaller velocity (5-20 mL min$^{-1}$) the retention of particles was clearly higher. Due to this, velocities were kept below 10 mL min$^{-1}$. The sorption onto the adsorber material took place under pronounced non-equilibrium conditions (RING, 2006).

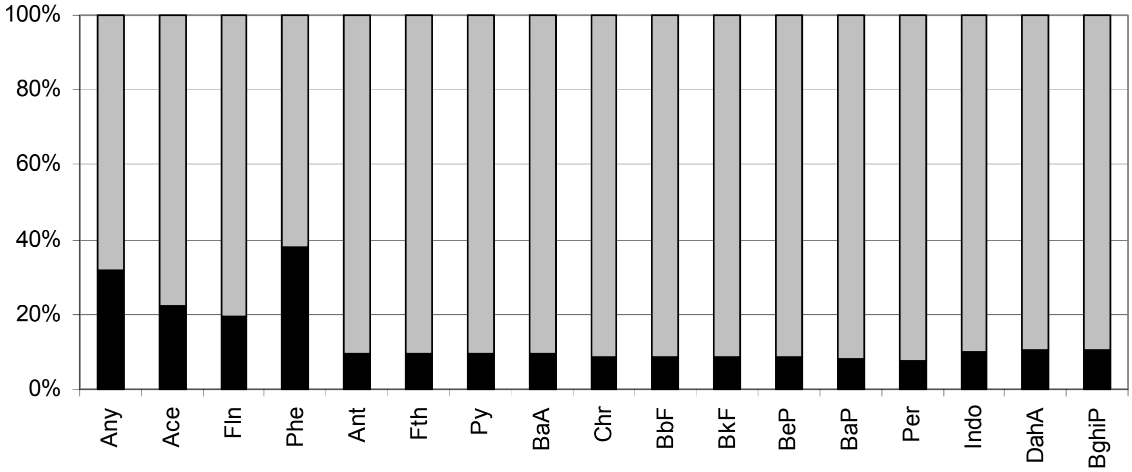

**FIGURE 7.2:** Percentage distribution on BT-h (black) and BT-v (grey). The sampling period for this cartridge was 15.9.-15.10.2005. This distribution shows that most PAHs stayed in the first cartridge.

### 7.3.2 Water Samples

The water samples showed high concentrations between 1-294 ng L$^{-1}$. A split-up of the five most common PAHs resulted in Phe (14 %), Fth (13 %), Ant (12%), Py (12 %) and BbF (8 %). Higher contents of PAHs were achieved when the discharge and its subsequent suspended load increased (Fig. 7.3). Most of the samples were collected during the snowmelts of 2005 and 2006 because the summer events did not change the behaviour of the spring as much as the snow melts did.

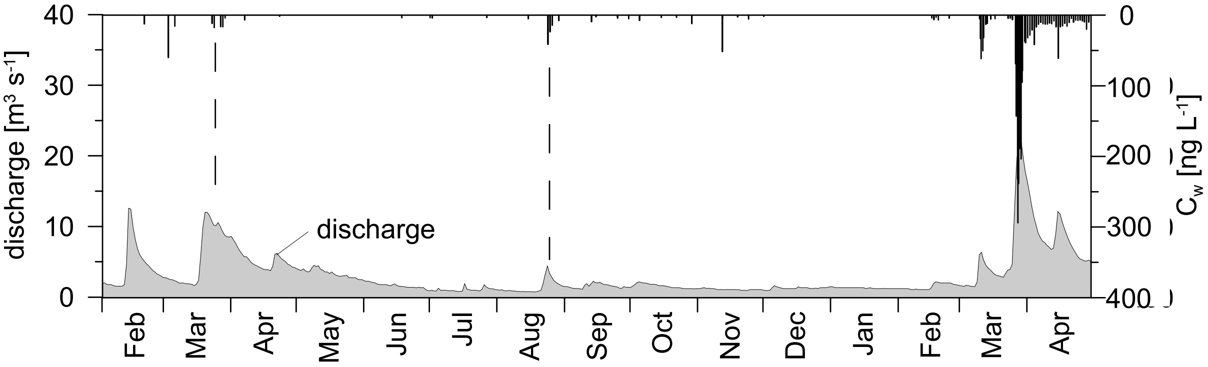

**FIGURE 7.3:** Discharge and concentrations of PAHs in the Blautopf Spring (February 2005 – April 2006).

The highest discharge was reached during the snow melt of 2006, when the spring discharge was more than 26 $m^3$ $s^{-1}$. During this event the highest concentration was measured (294 ng $L^{-1}$). Furthermore, the BaP limit for drinking water (10 ng $L^{-1}$ (TRINKWASSERVERORDNUNG, 2001)) was exceeded several times during this event with values ranging from 10 to 23 ng $L^{-1}$. The limit for BbF, BkF, Indo and BghiP (100 ng $L^{-1}$ (TRINKWASSERVERORDNUNG, 2001) was not exceeded, with the highest value recorded at 85 ng $L^{-1}$. This clearly shows that during normal discharge periods concentrations in groundwater are very low.

The distribution pattern of PAHs in the water samples was the same as the ones from the time integrated passive sampler. This means that the passive sampler worked well. Furthermore, both distribution patterns showed that the main transport process can be related to particles.

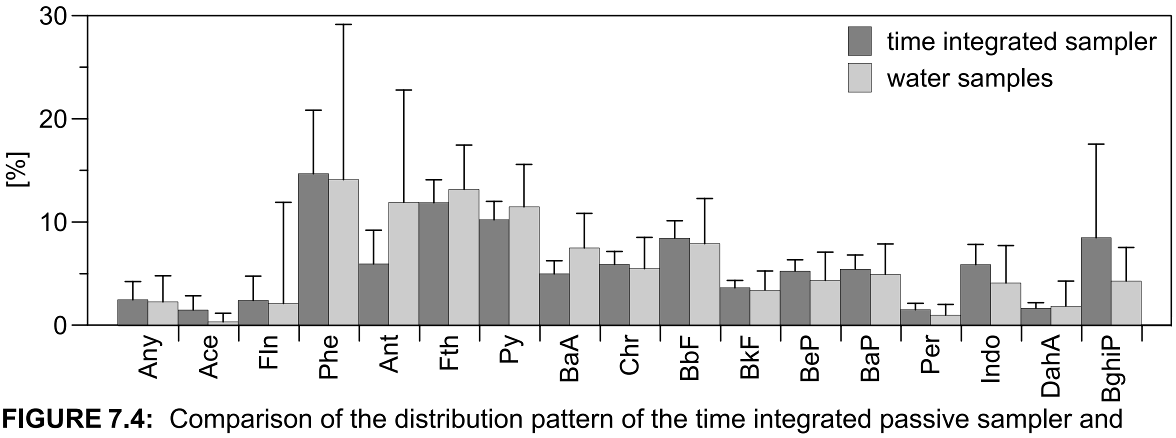

**FIGURE 7.4:** Comparison of the distribution pattern of the time integrated passive sampler and conventional water samples.

SIMMLEIT and HERRMANN (1987) detected PAHs in caves of the "Fränkische Alb" only during a snow melt event. They also recorded the highest BaP concentration during high water flows associated with high concentrations of suspended solids. This means that transport of PAHs is dominated by particulate transport. It can be assumed that these mobilised particles are deposited earlier and re-suspended in the system due to a higher flow velocity and that only a small part is supplied directly from the new event. This means that particles, which infiltrate with the seepage water, have accumulated in the huge karst system and will eventually be released over time. High discharge events can resuspend particles and transport them to the outlet of the system.

According to SELG et al. (2006), rain events and snow melts can be detected in the groundwater recharge of the Blautopf within a short retardation time of 1-2 days. They also assert that the increasing discharge is attributed to the piston flow effect: Water that flows out of the spring first is groundwater, which was stored in the system and pushed out by the pressure of the successively infiltrating event water. Therefore, the percentage of event water as a direct response to the spring discharge is very low, averaging around 8 % (BAUER and SELG, 2006). Otherwise, the direct discharge is below 1 % if there is no event.

Furthermore, BAUER and SELG (2006) reasoned that laminar (in contrast to turbulent) flow occurs in the network of fissures but not through the conduits. Thus, according to the low flow velocity there is enough time for the solutes to undergo numerous processes including retardation, degradation and dispersion. This can be a reason for the low concentrations in the spring during “normal” discharge.

In general, a rapid rise of water level at the spring indicates that sinks and spring are connected by a phreatic conduit system, which is able to transmit the pressure pulse rapidly to the spring (BIRK et al., 2004). However, prior to infiltrating into the conduits, the groundwater is stored and mixed in three possible areas: soil, epikarst and rock matrix.

### 7.3.3 Particle Associated PAHs Fluxes (Particles and Colloids)

The examined particles of the snow melt of 2005 showed concentrations of PAHs in the range between 4 and 19 mg kg$^{-1}$ [blank: < 3 mg kg$^{-1}$]. These are rather high values, which were not expected. It is considered that since the sampling volumes were only around 29 mg, that a relatively high sampling error, around 40-50%, should be regarded.

The most unexpected result of the particle-associated PAHs fluxes was that from the observed highest discharge event, the lowest PAHs concentration was measured. This could be caused by the higher turbulence of the spring water which mobilised other materials, like algae. In later observations, however, diluted concentrations of PAHs were recorded.

The water samples showed a different result from the particles. The concentrations of PAHs were higher with an increasing discharge due to a larger suspended load and higher percentage of event water.

According to ATTEIA and KOZEL (1997), particles as large as 4-5 µm can be considered as mobile in a karst system because they travel through the entire aquifer, and thus the PAHs which are associated with these particles are transported through the entire aquifer as well. ATTEIA and KOZEL (1997) additionally report that also larger particles can be suspended and transported through the karst aquifer system. Their presence is controlled by hydrodynamic processes.

In Fig. 7.5, the turbidity and the concentration of PAHs in the water, as well as the relation between turbidity and the suspended load, are presented. Increasing discharge is accompanied by an increasing turbidity (Fig. 7.6) and thus by an increase in particles (and colloids). Furthermore, this gives evidence that the particles were responsible for the increasing concentrations during high flow events. However, not all high turbidity events go along with higher concentrations of PAHs (open triangle). This finding is a sign for more complex transport behaviour of PAHs. Maybe the kind of particles plays a major role in this case. As known, soot particles are the main carrier of PAHs; perhaps if they are not present in the suspended load, there are also no PAHs. For the future, the particles during different turbidity events should be investigated.

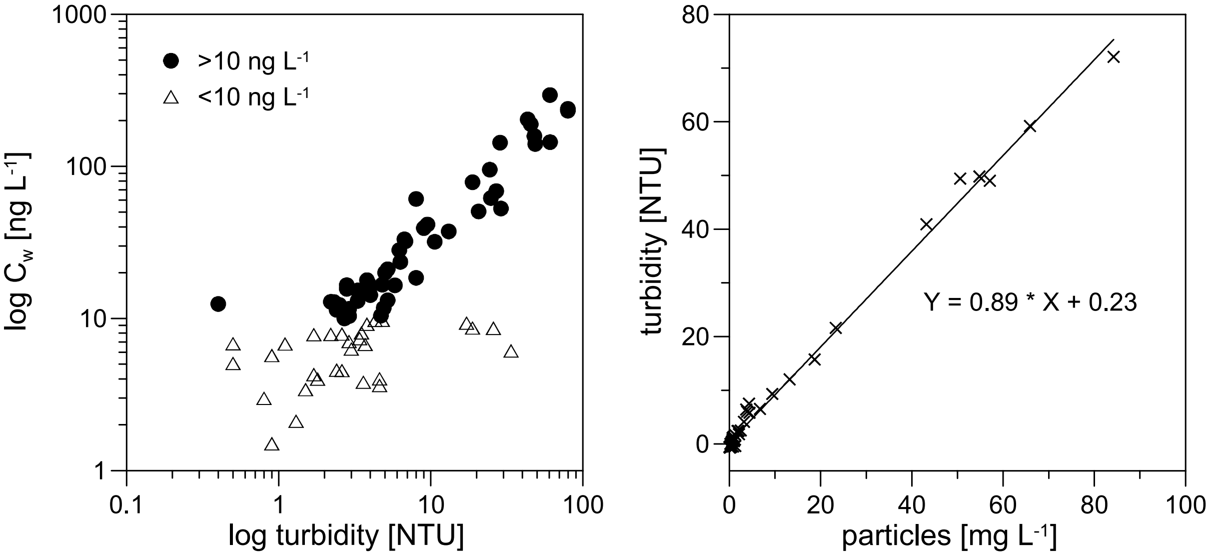

**FIGURE 7.5:** a) Relation between turbidity and $C_w$ in the Blautopf Spring and b) relation between particles (suspended load) and turbidity.

### 7.3.3.1 Output of Suspended Load

The suspended load was determined at different discharges by the collection of one litre samples. The results ranged between 0.1-84.2 mg $L^{-1}$, whereas the discharges were 1.5 $m^3$ $s^{-1}$ and 18 $m^3$ $s^{-1}$, respectively. TESSENOW (1980) found similar values, but his highest value was 179 mg $L^{-1}$ at 14 $m^3$ $s^{-1}$ (filter pore size 0.45 µm). He stated that most of the time (under normal conditions) the suspended load was smaller than 10 mg $L^{-1}$. This fits very well with the findings of this work, because during normal discharge there is almost no suspended load and the spring water looks clear.

The measured discharge values can be correlated with the measured values associated with the suspended load and turbidity. A large increase in discharge should be attributed to a wash-out effect, which will show an extremely high discharge followed by a subsequent sharp decrease. The turbidity, as measured by the data logger of the "Arbeitsgemeinschaft Blautopf" varied between 0-97 NTU. Negative values for clear water were replaced by 0. Random out-of-range values which were considered to be measuring errors were eliminated. At the end of the study period the values increased, which was caused by data logger (SCHOPPER, pers. com., Manager of the "Arbeitsgemeinschaft Blautopf"). The total output of suspended loads (particles) at the spring can be calculated with the derived equation based on data from the logger and the investigation of the suspended load in the Blautopf:

$$SL = \frac{T - 0.23}{0.89} \cdot Q \cdot t \qquad [7.1]$$

where SL is the suspended load [M], T the turbidity [NTU] and Q is the daily average discharge [$M^3$ $t^{-1}$]. For the turbidity and discharge, the daily mean was determined and used for the calculation. As discussed above, there is a correlation between turbidity and discharge, as was detected during the sampling periods. With increasing discharge the turbidity increases as well (Fig. 7.6).

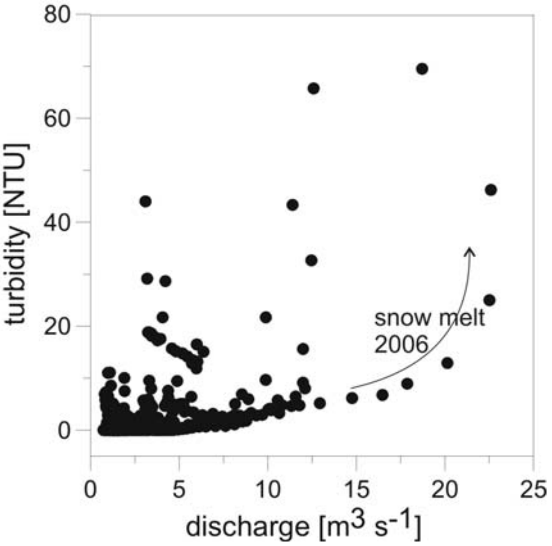

**FIGURE 7.6:** Relationship between discharge and turbidity in the Blautopf Spring.

Turbidity is a good parameter to distinguish between fast and slow water. Furthermore, a change in the electrical conductivity and temperature can also be an indicator for fast flow. Temperature decreases in winter and increases in summer with the arrival of the event water and has been seen to need a longer time period to stabilise to the pre-event value. MASSEI et al. (2003) give evidence that the evolution of the electrical conductivity seems to be linked to that of particle breakthrough.

### 7.3.3.2 Dissolved Organic Carbon (DOC)

The DOC varied in the Blautopf Spring between 0.8 and 2.4 mg $L^{-1}$. This corresponded with the values found in the different caves (Chap. 6). It was not possible to determine a clear trend between the DOC and the discharge of the Blautopf Spring (Fig. 7.7). Additionally, no seasonal cycle could be observed.

At the end of February, the DOC increased rapidly, but it was not possible to give a reason for this change.

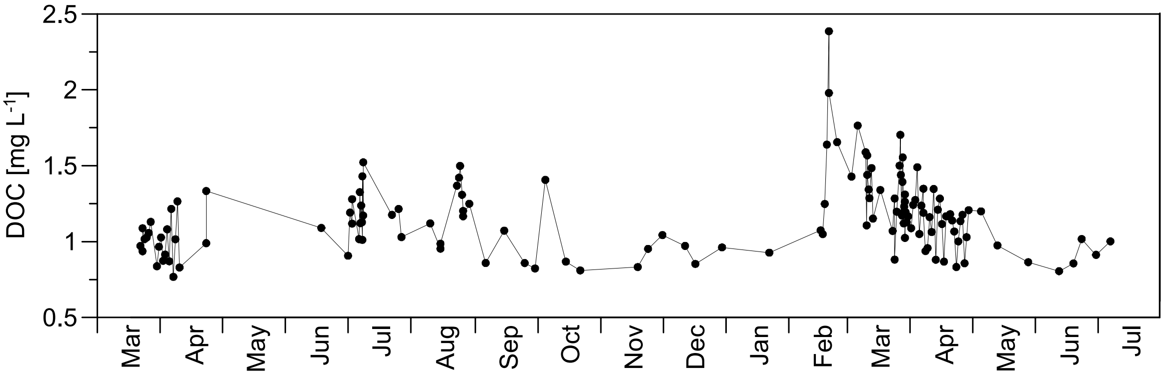

**FIGURE 7.7:** The DOC and the discharge in the Blautopf Spring from March 2005 till July 2006.

## 7.4 Summary

This study has shown the possibilities for investigating long-time periods, as well as short events like heavy rains or snow melts in karst systems by use of the two described sampling methods. The most important findings were:

- There is a low background concentration of PAHs in the Blautopf Spring (~10 ng $L^{-1}$). During "normal" flow conditions this value is fairly stable. However, during high flow events, such as snow melts, the concentrations of PAHs can increase dramatically. This increase can be correlated with a higher discharge and turbidity. But high turbidity events exist which show no elevated concentrations of PAHs.
- The German limit for drinking water for BaP was clearly exceeded during the snow melt of 2006, when the discharge was higher than 26 $m^3 s^{-1}$.
- It is necessary to use the two different sampling methods, because events can only be sampled by the established sampling with bottles. The time integrated sampler can not resolve short events with higher concentrations (snow melts, etc.). It gives good results for long term monitoring, provided that only the background information is important for

research. The sampling devices were concluded to supply good and stable results and were considered to be easy to handle and relatively inexpensive.

- It has also been concluded that the main transport mechanism of PAHs can be associated with particles. It could not be clarified if the particles came directly from the surface or if they had been re-suspended.

The main results from this part of the study were similar to those in Chap. 6. During low flow discharge there is currently no threat to the quality of the groundwater in the Blautopf Catchment. Furthermore, the results show that the greater part of PAHs stay in the system. In Chapter 4 it was shown that the soils are the most important storage space of PAHs.

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# CHAPTER 8

# INPUT-OUTPUT MASS BALANCE AND STORAGE OF PERSISTENT ORGANIC POLLUTANTS IN A KARST AREA

**Abstract**
Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental tracers of persistent organic pollutants (POPs). Input from the atmospheric deposition, accumulation in soil profiles, concentration in seepage water in caves, and finally the output through the karst spring was analysed. Thus, a input/output mass balance could be determined which helps to understand fate and transport of PAHs in catchments. We determined the PAHs fluxes in the four different compartments (atmosphere, soils, cave seepage and groundwater) of the karst catchment (Blautopf). This was realised with passive sampling devices that contained sorbing material (Amberlite™ IRA 743). No significant transport of PAHs during normal discharge in the spring was observed. The only times when PAHs were found at elevated concentrations in the groundwater was during high discharge events with turbulent flow. In the cave the concentration increased during winter when the drip rates were elevated. Therefore, the concentration in the seepage and groundwater was dominated by particle-facilitated transport. The mass balance indicates that over 82-94 % of POPs remain in the catchment and accumulate in the top soils and only little is transported into the groundwater during times of high and turbid discharge.

**Keywords:** PAHs, karst, mass balance, passive sampler, catchment

## 8.1 Introduction

PAHs are mutagenic, carcinogenic, teratogenic, and show a ubiquitous distribution as well. 16 PAHs have been identified as priority pollutants by the UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (1993), and have also been listed in the EUROPEAN LIST OF PRIORITY POLLUTANTS (2000).

PAHs are introduced into the environment by incomplete combustion of organic matter. Because of atmospheric emissions and long-range transports they are spread all over the world. The transport behaviour of PAHs, which belong to the semi-volatile organic compounds (SVOCs), depends on their physiochemical properties, like vapour pressure and temperature. Because they are semi-volatile, airborne PAHs can exist in both gaseous and particulate phase. The latter property is often associated with small carbon particles, which act as the most important carriers for PAHs (DACHS and EISENREICH, 2000; KLEINEIDAM et al., 1999; RÜGNER et al., 1999). Particularly, the less volatile 5- and 6 ring PAHs are bound to particles and the volatile 2- and 3 ring ones exist predominantly in gaseous phase in the atmosphere (HOWSAM et al., 2000).

From the atmosphere they enter the aquatic or terrestrial environment by wet and dry deposition and gas absorption. A continuous input of PAHs leads to accumulation in soils due to their sorption preference and their persistence. PAHs belong to the group of the persistent organic pollutants (POPs). A study for Great Britain showed that at least 90 % of environmental burden of PAHs is stored there in the soils, excluding contaminated sites (WILD and JONES, 1995). Via desorption the PAHs can change from the soil matrix into the aqueous phase (ALLEN-KING et al., 2002; SCHWARZENBACH et al., 1993). Hydrophobic contaminants can also absorb/associate with mobile dissolved organic matter (DOM) which facilitates a faster transport into the groundwater (KÖGEL-KNABNER and TOTSCHE, 1998). During fast transport in the seepage water sorption equilibrium may not be reached and the contaminants can be displaced into deeper zones (RAHMAN et al., 2004).

A number of studies have been conducted to investigate the input and output in different systems (MOTELAY-MASSEI et al., 2006). However, little is known about the vulnerability of karst systems regarding the risk of contamination by PAHs. Considering the fact that 25 % of the world's population use groundwater from karst aquifers as potable water (DREW and HÖTZL, 1999; FORD and WILLIAMS, 1989), more investigation should be done. Furthermore, the soil cover is thin and thus the protection and buffer function is rather low. This means that contaminants can enter the karst aquifer more or less unimpeded and the high groundwater velocity can be another established risk factor.

Contaminant environmental fate models can help to estimate loading and long-term fate of compounds such as PAHs and to identify key data gaps in understanding these processes (GREENFIELD and DAVIS, 2005; MACKAY et al., 1994). To better understand fate and transport of PAHs, it is important to study the behaviour in different media. Therefore, a detailed catchment study was conducted in this work, including all important media, like atmosphere, soils, seepage water and groundwater. It is difficult to establish experiments in the field which consider all transport pathways and processes. For instance, typical tracer tests in karst systems only include the fast conduits because the tracer is usually added in sinkholes. For this reason we have chosen PAHs which are ubiquitous for the whole catchment. Furthermore, snow melts and heavy rain events can be used as natural events which can mobilise water which is stored in the karst aquifer.

The purpose of this study was i) to develop a method for quantification of fate and transport of organic pollutants at the field scale from atmosphere to soil, seepage water and spring, ii) to establish a mass balance from atmosphere to the outlet of the system and iii) to predict pollution trends in the different environmental compartments.

## 8.2 Materials and Methods

### 8.2.1 Sampling Sites

The field site is located on the “Schwäbische Alb” which is part of the cuesta landscape from Southern Germany. The geological formation is dominated by the Upper Jurassic, which is build up with layered and massive limestone. The limestone is fractured and shows large karst features.

The Blautopf Catchment covers a total area of around 165 $km^2$ (BAUER and SELG, 2006). It is located west of "Blaubeuren", where the Blautopf (48° 24' 57" N, 9° 47' 2" E) has its source (Fig. 2.1). The latter is the second largest karst spring in Germany, with a maximum discharge of 32 $m^3 s^{-1}$. There is only one other small spring nearby (“Gerhauser Quelle”), which was neglected in this study. Several tracer tests have been accomplished in the catchment area. They came up with peak velocities up to 350 $m h^{-1}$ (VILLINGER and UFRECHT, 1989), whereas the average flow rate was around 100 $m h^{-1}$ (GROSCHOPF, 1957; VILLINGER and UFRECHT, 1989). The hydrology of the system is described elsewhere (VILLINGER, 1978).

In the catchment there are more than 50 caves, of which the "Laichinger Tiefenhöhle" (LTH) was chosen for this study. It is a show cave and located in the middle of the catchment area. The sampling points are around -33 m above the surface.

The area is very rural, around 31 % of the area is covered with forests and more than 60 % is agricultural land (KÖBERLE, 2005). Soils are derived particularly from weathered limestone, which are very heterogeneous (GIEßL and HURLE, 1984). The main soil type in the Blautopf catchment is a "Rendzina" (rendzic leptosol), others are "Braunerde" (cambisol) and "Kolluvisol" (redeposited soil of high thickness).

The catchment is located in the temperate zone with an annual average temperature of 7 °C and an annual precipitation of 1057 mm (POSTIGO REBELLO, 2006).

### 8.2.2 Sample Collection

#### 8.2.2.1 Atmospheric Deposition

Bulk atmospheric deposition samples were collected at three sites within the catchment. The sites have been chosen because of the different deposition conditions, in a village, a forest, and an open territory. The passive samplers (GOCHT et al., 2006; GOCHT et al., 2007; MARTIN and GRATHWOHL, 2002) were installed 1.2 m above the ground. The sampler consisted of a stainless steel box, containing a glass funnel and a glass cartridge filled with an adsorber material made of polystyrene (15 g; Amberlite™ IRA743, Fig. 3.1). It continuously collects wet and dry deposition (particulate and gaseous phase; collection area = 0.049 $m^2$). Before using the IRA, it was cleaned by means of Soxhlet extraction for 20 h with acetone and dried at ambient temperature. After cleaning it was stored in solvent-rinsed glass jars in the dark. In the field the deposition samples were deployed for two months. The sampling period was from June 2004 to June 2006. The main reason for employment of passive samplers is that they do not require any electricity or any other power source to operate and accumulate chemicals over extended time periods (BARTKOW et al., 2005).

#### 8.2.2.2 Seepage Water

The seepage water was sampled in one cave (LTH) at two locations side by side. One was installed beneath a fast dripping place (LTH II) and the other under a slow one (LTH I). To collect the infiltrating water the same cartridges and adsorber material were used as those within the atmospheric deposition. The water was collected with funnels connected to cartridges (only by gravitation). At the outlet of the cartridge there was a closed bucket to collect the water. The bucket had to be emptied every 1-2 weeks. However, the sampling point LTH II overran almost every time, so no exact volume is known and the given concentrations are just maximum values.

The cartridges were exchanged when more than 50 L of seepage water was sampled, and the water volume was recorded to allow calculation of the respective concentrations of PAHs (note that the temperature in the caves is fairly constant at 8°C over the year and thus evaporation of water from the open surfaces in the buckets is negligible). The funnels were cleaned with acetone soaked glass wool, which was also analysed in the lab (together with the adsorber material). This method was efficient to clean the sampler.

#### 8.2.2.3 Groundwater

Concentrations of PAHs in the groundwater were measured in the karst spring using time integrated sampler. We used 2 special extraction cartridges in sequence made of stainless steel filled with IRA (~13 g) and a silica sand filter at both ends, as well as three sieves with a mesh aperture of 0.75 mm (at the endings and between the two cartridges). The cartridges were installed in the spring and connected to a peristaltic pump by PTFE tubing. This system sampled the water in the spring continuously with average flow rates of 10 mL min$^{-1}$. To make sure that no breakthrough of PAHs occurred, two cartridges in series were used.

Because of variations in the flow rate, due to different reasons like tube aging, the determined volumetric flow rates were calibrated before and after sampling. On the basis of the flow rates the concentration in ng L$^{-1}$ per cartridge was calculated.

The tubes were changed every two months to ensure the quality of the sampling. In summer they became overgrown with algae and additionally snails settled in the tubes. During winter they froze as the temperature was close to -5 °C and lower. When the tubes were completely frozen (which happened several times) the total system was stopped and restarted at warmer conditions.

#### 8.2.2.4 Water Samples

From March 2005 to 2006, additional water samples were taken in the cave and the spring. In the cave the one or two litre bottles connected with a funnel made of stainless steel were disposed near the sampler. Every time the buckets from the sampler were emptied, the bottles were changed. A disadvantage of this sampling procedure was that the water in the bottles overflowed almost every sampling period. This means that the exact water volume could not be specified. Concerning the particles it would have been important to know the exact amount of water, because they could settle down and thus increased the contents of

PAHs. Larger containers could not be used, because the transport would have been impossible due to narrow shafts and ladders in the cave system.

The water in the Blautopf was taken in a depth of 20 cm above the weir. At this place, there is always a flow and it can be accepted that it was fresh discharged water. The samples were stored until analysis at 4 °C in the dark.

### 8.2.3 Analysis

All samples were analyzed for 17 PAHs: (Ace) acenaphthene, (Any) acenaphthylene, (Fln) fluorene, (Phe) phenanthrene, (Ant) anthracene, (Fth) fluoranthene, (Py) pyrene, (BaA) benz(a)anthracene, (Chr) chrysene, (BbF) benzo(b)fluoranthene, (BkF) benzo(k)fluoranthene, (BeP) benzo(e)pyrene, (BaP) benzo(a)pyrene, (Per) perylene, (DahA) dibenz[a,h]anthracene, (Indo) indeno[1,2,3-cd]pyrene, (BghiP) benzo[ghi]perylene. All ΣPAHs concentrations listed in this paper are based on the sum of these 17 compounds.

The adsorber material was extracted in a luer taper syringe (100 mL) adding 200 mL acetone in four steps. Each step took 2 min with 50 mL solvent, respectively. Subsequently, the surrogate standard was spiked into the extract and then cyclohexane (10 mL) and Millipore water (2 L) were added. Afterwards it was shaken for one hour and stored for one day in the dark. Finally the cyclohexane was extracted and concentrated to ~150 µL under nitrogen.

Subsequent to the extraction, the extracts contained a lot of co-extracted compounds, which lead to difficulties during GC-MS analysis. Hence, dark coloured extracts were purified using an alumina-silicic column (1:1) and different isohexane (ISO)-dichloromethane (DCM) solvent mixtures to eluate the sample (30 mL pure ISO, 5 mL 9:1 (ISO:DCM), 20 mL 4:1). Following that, the extracts were concentrated on a rotary evaporator to about 150 µL.

PAHs were analyzed on a Hewlett-Packard 6890 gas chromatograph equipped with a mass selective detector (HP-5973) using a DB-5 capillary-column (30 m x 0.25 mm). Standards (20 mg $L^{-1}$) with five deuterated PAHs surrogates (Nap-d8, Ace-d10, Phe-d10, Chr-d12 and Per-d12) were added to the sample extract and used for the quantification of PAHs. A diluted standard containing the 16 PAHs and the 5 deuterated surrogates was measured to calculate the relative response factors.

### 8.2.4 Turbidity, temperature and conductivity

The “Arbeitsgemeinschaft Blautopf” installed in May 2004 a data logger in the Blautopf. This logger (model 6920, company YSI Incorporated, Ohio, USA) was fixed in the “Blauhöhle” at a depth of -31 m and around 70 m away from the entry in the underwater cave.

It recorded the water level, the turbidity, the conductivity, and the temperature. For more details please see SELG et al. (2006).

### 8.2.5 Quality Control and Assurance

It was necessary to undertake precautions to avoid sample cross-contamination. To achieve this, all employed materials were cleaned with acetone and only used for this investigation. All solvents and standards were tested for the target component regularly. Additionally, the recovery rate and the reproducibility were checked with internal standards (Fth-d10).

For each sampling period a field blank was taken. The samples and the corresponding blanks were analysed together. The result of all measured samples can be found in the appendix. All blank values are shown in the text in brackets []. The blanks were useful to check for background contamination or any other possible influences caused by transport or in the laboratory.

## 8.3 Results and Discussion

### 8.3.1 Input into the Catchment (Bulk Atmospheric Deposition)

The atmospheric deposition rates (gaseous and particulate) were in the range from 56 and 1983 ng $d^{-1}$ $m^{-2}$ [blank: < 4 ng $d^{-1}$ $m^{-2}$] whereas the village showed generally the highest and the forest the lowest values. Leaves in the sampler were not considered in the analysis. The weighted deposition for the three compartments in the first/second year were 590/484 ng $d^{-1}$ $m^{-2}$ (village), 187/177 ng $d^{-1}$ $m^{-2}$ (forest) and 254/195 ng $d^{-1}$ $m^{-2}$ (open territory) [23/13 ng $d^{-1}$ $m^{-2}$]. The deposition rates for the two year sampling period are displayed in Fig. 8.1. The deposition rates of the carcinogenic PAHs like BaA, BbF, BkF, BaP, DahA and Indo (2005) showed values between 14/12 and 328/260 ng $d^{-1}$ $m^{-2}$ [< 1 ng $d^{-1}$ $m^{-2}$]. These values constitute between 8-38 % of the percentage of the total PAHs. The average of the PAHs distribution pattern shows that Phe (22 %) was the dominating substance followed by Fth (17 %), Py (12 %), BbF (7 %) and Chr (7 %). One of the carcinogenic PAHs (BbF) is the fourth most commonly deposited.

All locations showed seasonal fluctuations in their concentrations with 2-4 times higher deposition rates during winter, a result that coincides with other studies (BRUN et al., 2004; HALSALL et al., 1997; MOTELAY-MASSEI et al., 2003). The most pronounced difference was found in the village. This shows directly the effect of domestic heating during the cold season (BRUN et al., 2004). The main input of PAHs was associated with particles as indicated by the distribution pattern, where the HMW-PAHs dominate. FERNÁNDEZ (2003) and FERNÁNDEZ et al. (2005) also found atmospheric particles to be the main transport media.

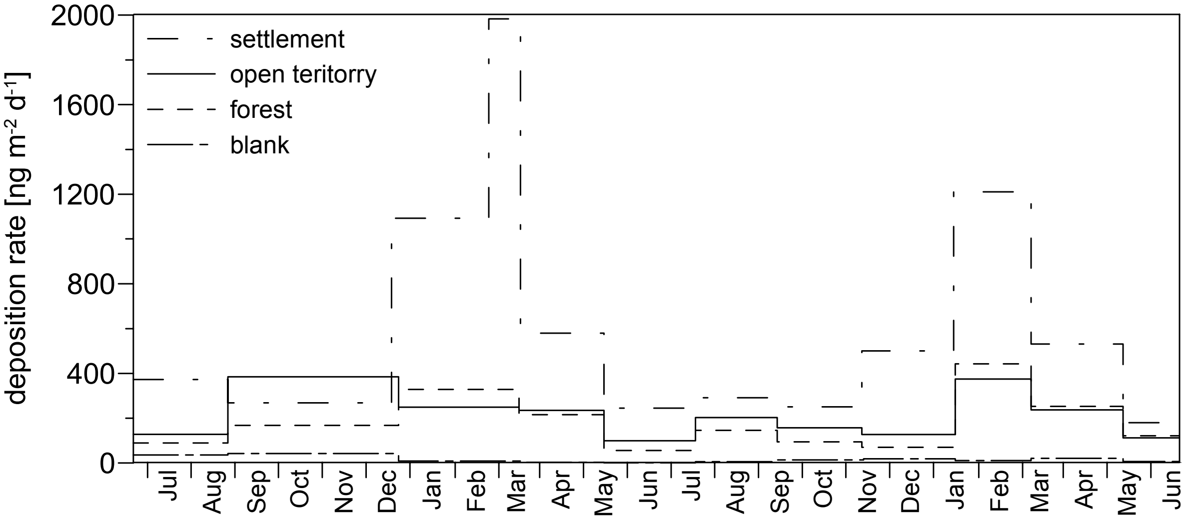

**FIGURE 8.1:** Atmospheric deposition rates [ng $d^{-1}$ $m^{-2}$] from June 2004 till June 2006.

## 8.3.2 Transport Processes (into and) in the Groundwater

Substances can reach the groundwater, if some essential conditions are fulfilled. Two of them are persistence against degradation and mobility or solubility in water. Furthermore, the soil cover and its permeability play a major role. Due to the thin soil cover, sinkholes, and open shafts, there are preferential pathways for infiltrating water.

### 8.3.2.1 Seepage Water

While the concentrations of PAHs in the seepage water did not vary a lot, the values for LTH ranged between 2–371 ng $L^{-1}$ [n.d.]. The higher concentrations were always found in samples that were located under the slowly dripping seepage water. This is presumably due to less dilution in fast flowing seepage water. Altogether drip rates did not remain constant during the monitoring, but instead changed with the seasons. In summer the rates were lower due to less precipitation and higher evaporation on the surface. During winter, and especially in spring during snow melt, they were highest. The five most common PAHs in the distribution patterns were Fth (16 %), Py (12 %), Phe (11 %), BbF (9 %) and BaA (8 %). Low-molecular (LMW) as well as high-molecular PAHs (HMW) were represented in the water. This shows the existence of two different transport processes in water, one dissolved and the other associated with particles.

Additional water samples with conventional water sampling using 1 L amber glass bottles showed values in the range of 4–34703 ng $L^{-1}$. In consideration of the distribution pattern, it was almost the same as with the time integrated sampler: Fth (18%), Phe (15 %), Py (13 %), BbF (9 %) and BaA (8 %).

In this study it was important to get information about the influence of heavy rain events and snow melts on the vadose zone and groundwater. For the seepage water a good correlation between concentration and events was given. There were two main events, both snow melts in March. They were recognisable in the conventional water samples as well as in the time integrated sampler, because the ∑PAHs increased obviously during these periods. Actually, during the snow melt in 2005, the BaP concentration in the time-integrated passive sampler exceeded the German limit for potable water (10 ng $L^{-1}$) and reached 30 ng $L^{-1}$ (Fig. 8.2). Furthermore, this limit was also exceeded with the conventional water samples. Maximum concentrations were up to 2.5 µg $L^{-1}$, which is 250 fold over the limit for BaP. This extreme value was observed during the snow melt of 2006. Additionally, it could be observed that the BaP content, as well as the content of ∑PAHs, was generally higher during winter, when the drip rates were also higher. These water samples represent maximum values, because the real amount of water was not known exactly and the particles that are responsible for the transport of PAHs might have accumulated in the sample bottles during overflown periods. However, this indicates that an increased transport of PAHs during high discharge events, especially snow melts in a karst area, occurs.

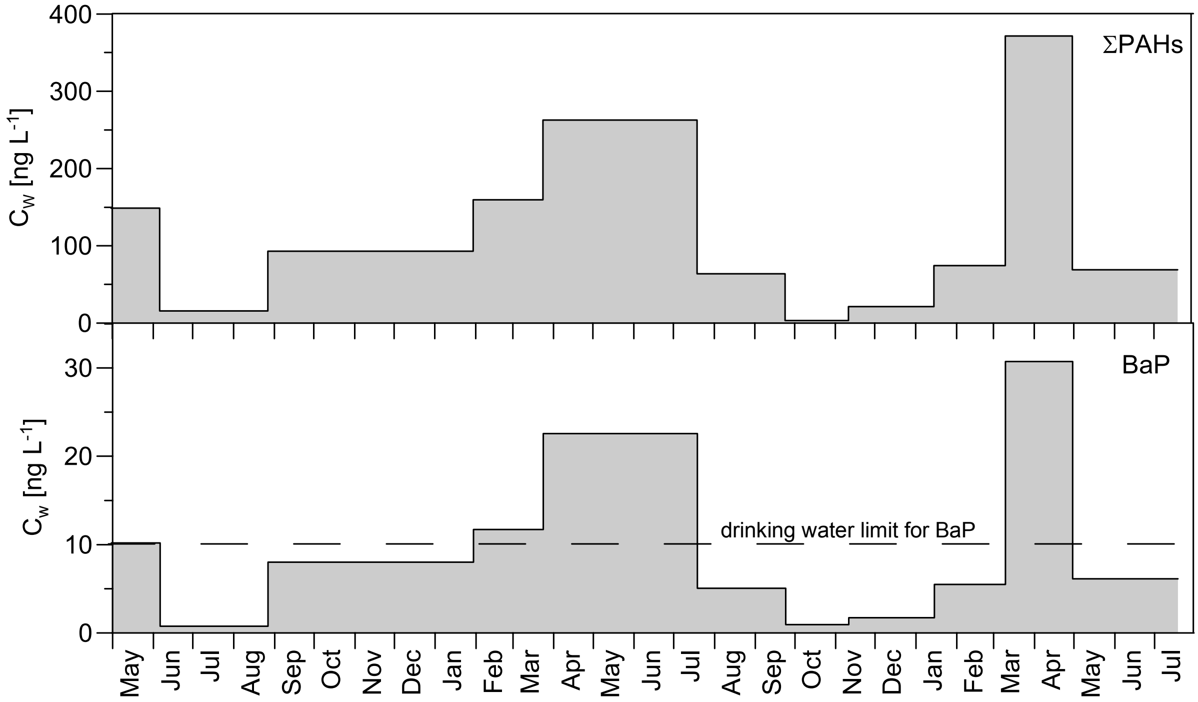

**FIGURE 8.2:** The upper graph shows ΣPAHs in the TIpS of LTH I (seepage water) and the lower graph shows the BaP concentration (LTH I) from May 2004 till July 2006.

### 8.3.2.2 Groundwater from the Spring

The concentrations of PAHs in the spring samplers were always very low. The values were lower than 56 ng L$^{-1}$ for all three cartridges (BT K1-K3). However, most of the passive samplers still showed values well above the detection limit due to the accumulative properties of the sampler. The distribution pattern showed that Phe (15 %), Fth (12 %), Py (10 %), BghiP (9 %) and BbF (8 %) were the prevalent PAHs in the spring.

The long-time monitoring system could not resolve short events with higher concentrations (snow melt, heavy rain events, etc.), because only the average concentration for the whole sampling period was calculated. However, short events can be determined using the conventional sampling system. In general, the dilution effect leads to generally lower concentrations in the passive samples during peak events compared with conventional sampling.

The water samples directly taken from the spring showed higher peak concentrations up to 294 ng L$^{-1}$. Higher concentrations of PAHs occurred when the discharge and the suspended load (turbidity) in the spring increased. Summer events did not affect the concentration of PAHs as much as the snow melts did. A distribution into the five most common PAHs resulted in Phe (14 %), Fth (13 %), Ant (12 %), Py (12 %) and BbF (8 %).

In Fig. 8.3 a comparison of the water samples and the results from the time-integrated passive sampler (TIpS) is presented. Both methods agree very well in March/April 2006. Here the concentrations reached values of 294 and 56 ng L$^{-1}$ in the water samples and the TIpS, respectively. This snow melt event was the strongest in several years; it almost reached the maximum water discharge from the year 1989 (~32000 L s$^{-1}$).

A mean baseline concentration for the spring, calculated based on the data of the conventional water samples and the discharge, came up as 7 ng L$^{-1}$. The arithmetic mean of the passive sampler is 5 ng L$^{-1}$ (n=42) and the one from the conventional water samples is 31 ng L$^{-1}$ (n=105). The latter mean is higher due to the privileged sample frequency during events. Increased turbidity was correlated with increasing contaminant output. This indicates that the PAHs are transported especially in association with particles. Thus the dissolved fraction plays only a minor role for the flux of PAHs in groundwater.

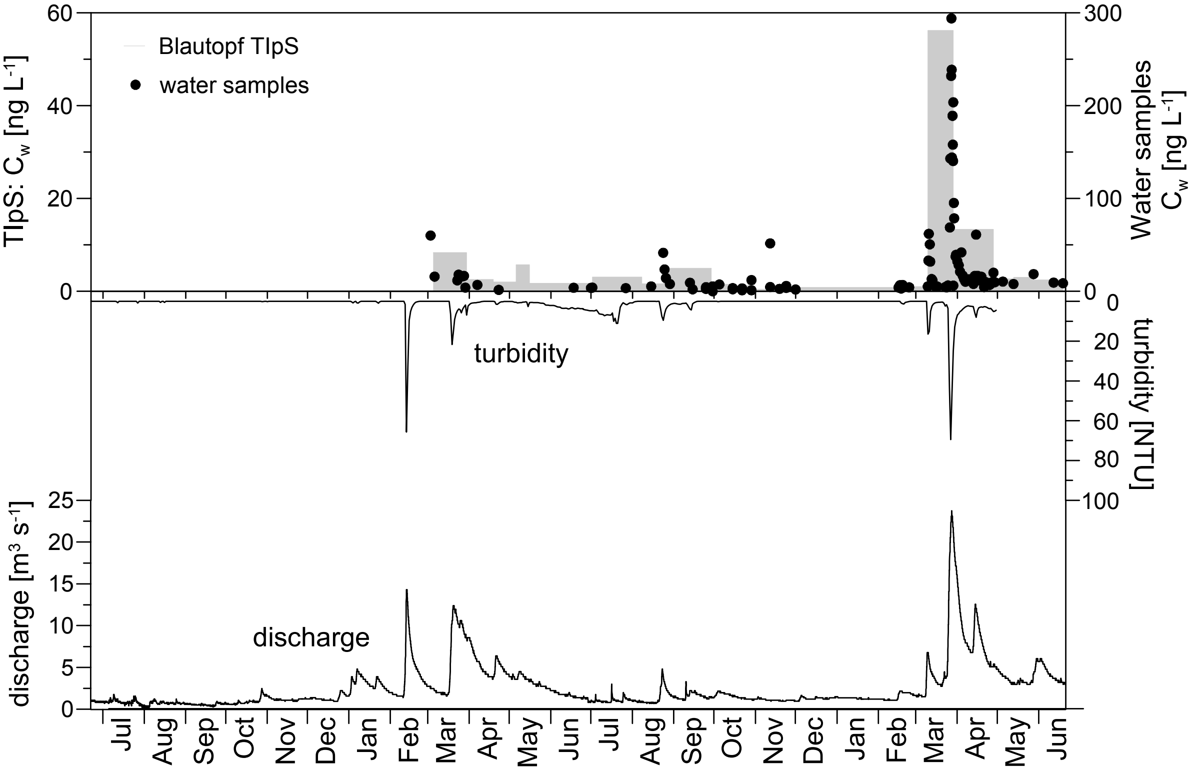

**FIGURE 8.3:** Concentrations in the groundwater [ng $L^{-1}$], determined with the time integrated passive sampler (TIpS) and in conventional water samples from March 2005 till July 2006. Please note the different scales on the y-axes.

## 8.3.3 Mass balance of the Catchment

### 8.3.3.1 INPUT: Bulk Atmospheric Deposition

Mass balances allow assessing fate and transport of pollutants at the catchment scale. For this purpose the measured deposition fluxes of the atmosphere can be used to calculate the input $I_c$:

$$I_c = n \sum_{i=1,2,3}^{c} \Phi_i \cdot A_i \qquad [8.1]$$

$I_c$ is the atmospheric input into the catchment area, $\Phi_i$ denotes the daily deposition flux [$M\,L^{-2}\,t^{-1}$], $A_i$ the area [$L^2$] and n the number of days [t]. Because the area is rather huge, some simplifications had to be done. The three locations (settlement, forest, and open field) were assumed as representative for the working area. This can be done, because it is known that the deposition rates are rather constant. A simplified land use of the catchment is given by settlements with 8 % (~13 $km^2$), open territory with 61 % (~98 $km^2$) and forest 31 % (~48 $km^2$) (KÖBERLE, 2005).

During the first year the input of PAHs by atmospheric deposition was 15.2 kg [1.4 kg]; for the carcinogenic PAHs it was 3.9 kg [n.d.]. In the second year the input was slightly less and accounted for 12.4 kg [0.7 kg].

BRUN et al. (2004) found a decreasing trend concerning the deposition rates of PAHs in the Canadian arctic of 65–7 $\mu g\ m^{-2}\ a^{-1}$ from 1989 till 2000. The yearly atmospheric deposition fluxes for our study reached 55–216 $\mu g\ m^{-2}\ a^{-1}$ for the different compartments. All fluxes were 8-30 times higher than the ones from 2000 from BRUN et al. (2004).

#### 8.3.3.2 OUTPUT: Groundwater

The PAHs fluxes in the spring were used to calculate the output of the system for a whole year:

$$O_C = C_W \cdot D \cdot n \qquad [8.2]$$

where $O_c$ is the output of PAHs of the catchment [M], $C_w$ the average concentration of PAHs in the spring water [$M\ L^{-3}$], D is the average, daily discharge of the spring during the sampling period [$L^3\ t^{-1}$] and n the number of days [t]. For the discharge the daily average values were used. These data were provided by the "Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg" (Karlsruhe).

The output at the spring was 0.9 kg in the first and 2.2 kg in the second year. This higher value in the second year can be associated with the extreme snow melt event in March and April. Generally all events (high flow and snow melts) over the whole year contributed 58-73 % to the total output of PAHs. This indicates that events are the most important contributors regarding output of pollutants. Particles are especially important regarding the output of contaminants.

The mass balance shows that the input is definitely higher than the output. Between 82 % and 94 % PAHs stayed in the system and only a small percentage left the catchment area. In this case the soils are the most important accumulation compartment, as was also found by GOCHT (2005). GREENFIELD and DAVIS (2005) figured in their mass balance model that 80–90 % of total loss of PAHs depends on degradation in sediments. For the LMW-PAHs volatilization accounted 10 % of total loss.

A comparison of the three different distribution patterns yields no difference in the PAHs signal from the atmosphere to the spring (Fig. 8.4). This indicates that all input and output is dominated by particle associated PAHs. According to SHEVENELL and MCCARTHY (2002) a mobilisation of colloids in karst areas, which can transport pollutants, depends on hydrological processes like heavy rain events (thunderstorms). ATTEIA et al. (1998) show that particles are retarded because of aggregation followed by sedimentation or sticking to conduit walls. These particles appear in the spring only during high flow events as a consequence of resuspension. These two possibilities are documented at the Blautopf, because higher concentrations were only observed during high discharge events, when the turbidity was high.

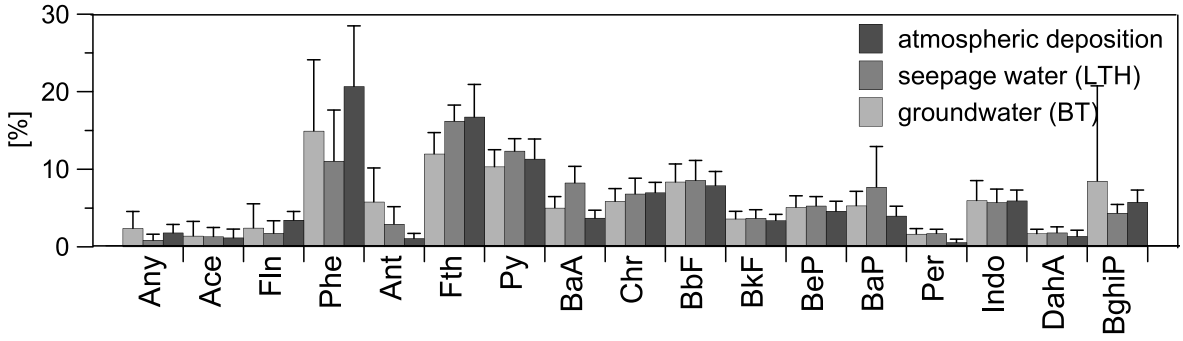

**FIGURE 8.4:** Comparison of the distribution pattern from the atmospheric deposition, seepage water and groundwater.

Average aquifer permeability is given with 5 x $10^{-3}$–5 x $10^{-5}$ m $s^{-1}$ for the deep karst (VILLINGER, 1997). But it is also documented that huge differences ($10^{-1}$-$10^{-9}$ m $s^{-1}$) can be found in close contact to each other. This means if the contaminated water enters a fast conduit it will reach the spring very fast due to the high velocities and no sorption or degradation can take place.

Destroying the soil cover should be avoided because this is the main buffer for PAHs. But the storage in the soil also has disadvantages. According to SIMONICH and HITES (1995), pollutants can enter plants via the roots and be translocated by the xylem. Thus this uptake is the first step through the food chain which finally result in a health risk (MCLACHLAN, 1997).

QUENTIN et al. (1973) assumed already that fissure and karst aquifers (on the "Schwäbische Alb") do not afford enough protection against the distribution of organic environmental chemicals. They detected lindane in drinking water close to a lindane hazard.

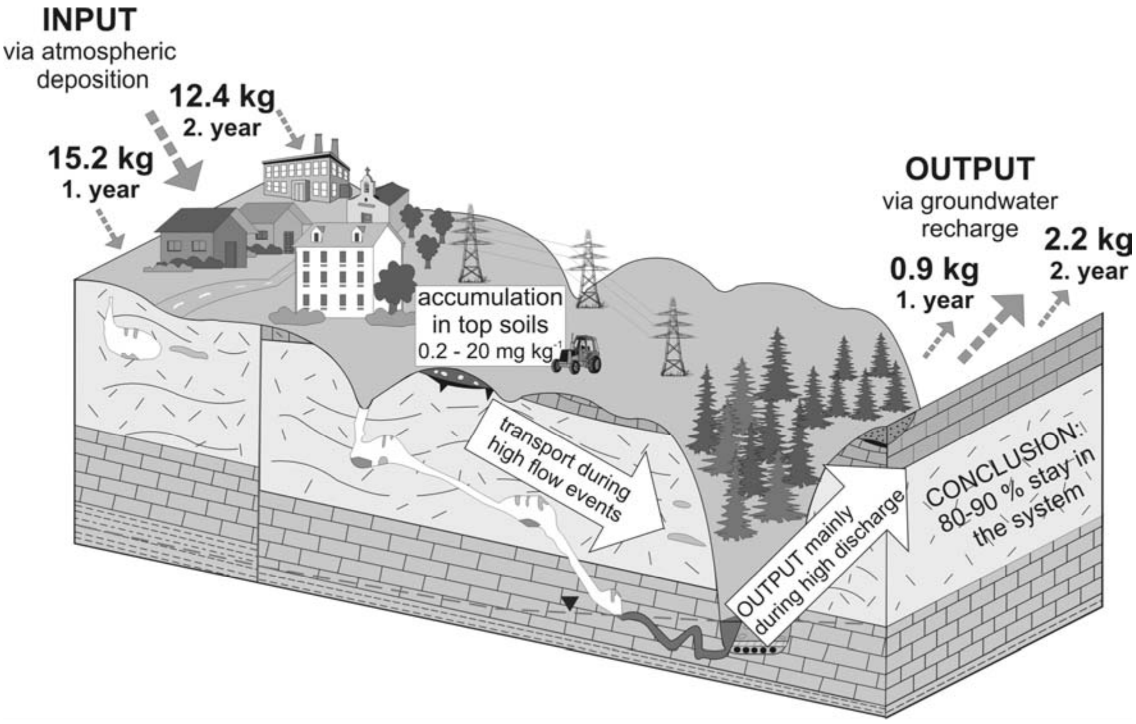

**FIGURE 8.5:** Summary scheme of the mass balance in the Blautopf Catchment.

## 8.4 Summary

The field site investigation provided a methodology with which it was possible to follow the pollutants from the atmosphere into the groundwater. The main results were:

- About 90 % of PAHs do not reach the groundwater and accumulate in top soils.
- Ca. 50 % of all output of PAHs is associated with events like snow melts and high flow.
- Input into and transport through the karst system is dominated by particle-associated PAHs. Particulate transport was the main process to move PAHs from the surface to the spring. This was proved by a correlation of distribution patterns from the different compartments (atmosphere, seepage and groundwater). However, it could not be determined if the particles were re-suspended or directly delivered from the surface along preferential flow paths. A pressure pulse mechanism (e.g. piston flow effect) or cryofocus are the main factors controlling the mobilisation of particles because they only appear in connection with higher flow rates. This means that the stored water in the soil, epikarst, and unsaturated zone was pushed downwards and the new infiltrated water displaced the older water. Subsequently, the unsaturated fissures in the rock matrix were flooded and connected, and the flow rate increased. The epikarst was probably the main supplier to these pathways. However, part of the new infiltrating water bypassed the storage zones along preferential flow paths. Finally the system started to empty the fissures, so they lost their connection to each other and the concentrations decreased again.

- There was one exceedance of the German limit of drinking water during a snow melt event in 2006 in the TIpS. In the water samples the limit was exceeded very often, because the particles had accumulated. It could be determined that the ∑PAHs concentration increased mainly during high discharge events and in winter, when the dripping rates in the cave were high. This shows that there is an endangering of the groundwater during events with high discharge. However, the concentrations in the spring were not as high as the ones from the seepage water.
- The method used was efficient and supplied good results with comparably low costs. The time-integrated passive sampler can be used for long term monitoring, in case events do not play a major role in the investigation. Otherwise, the sampling periods should be shortened.

The complexity of the processes in a karst aquifer makes it difficult to predict the fate and transport of pollutants. This work indicates that there is a large storage capacity for pollutants because the greater part of the input via atmosphere does not reach the output.

For further work the main focus should be aimed at investigations in the soil, the matrix porosity, and the epikarst zone.

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# CHAPTER 9

# MIXING AND TRANSPORT WATER IN A LARGE KARST CATCHMENT WITH STABLE ISOTOPES: FROM PRECIPITATION VIA SEEPAGE WATER TO THE SPRING

**Abstract**

One of the best-known and second largest karst areas in Germany (Blautopf Catchment) offers a unique access to waters of the unsaturated zone through a large cave system. The catchment was investigated with stable isotopes ($^{18}O/^{16}O$ and D/H ratios) in precipitation, using seepage- and groundwater as tracers for water flow, mixing, and storage. The precipitation showed a distinct seasonality with $\delta^{18}O$ values between -2.9 and -24.6 ‰ during summer and winter, respectively. However, the isotope signals in seepage water in the caves as well as the discharge were almost completely buffered and ranged around an average $\delta^{18}O$ value of -10 ‰. This value also closely matched the long term average of local precipitation of –9.3 ‰. The homogeneous isotopic composition of the Blautopf Spring was against expectation for its highly variable discharge (0.3 to 32 $m^3$ $s^{-1}$) that is typical for a fast responsive karst system. These isotopic similarities could be explained by nearly complete mixing of the water already in the vadose zone. The data set therefore presents a case study to narrow down zones of mixing in karst catchments. It also confirms the minor role of the fast conduit system in the water balance of the Blautopf Catchment.

**Keywords:** Karst, epikarst, catchment, stable isotopes, phreatic and vadose zone, Schwäbische Alb (Swabian Alb)

## 9.1 Introduction

Understanding of water pathways and movements in the vadose zone is a prerequisite for evaluation of the risk for groundwater pollution. In karst areas such evaluations become particularly important as about 25 % of the world's population rely on karst sources for potable water supply (FORD and WILLIAMS, 1989). A brief classification of karst systems is summarised by CRUZ JR. et al. (2005), GENTY & DEFLANDE, (1998) and MANGIN (1974) who define three main flow compartments:

1. the non-karst recharge area consisting of soils or non carbonaceous bedrock
2. the epikarst and
3. the saturated zone.

Next to soils and the vadose zone for mixing, the influence of the epikarst was recently investigated in more detail as it is assumed to play a major role in mixing of waters (AQUILINA et al., 2006; CLEMENS et al., 1999; PERRIN et al., 2003; SAUTER, 1995). According to MANGIN (1973), epikarst is a perched saturated zone above the groundwater table that stores part of the infiltrated water. In order to describe the variable flow character of karst systems, it also is necessary to consider the conduits that are embedded in the fissured-porous matrix (KIRALY, 1998; LIEDL & SAUTER, 1998; 2000). However, since the latter are assumed to play a minor role in karst water balances, ubiquitously distributed tracers such as stable isotopes of water can help to assess risk of diffuse pollution for catchment-wide water recharge considerations. As opposed to focused tracer tests with dyes or salts, more widely distributed tracers such as stable isotopes help to characterize such diffuse infiltration. This works if stable isotope changes in space are homogeneous and altitude effects can be assumed to be minor (CLARK & FRITZ, 1997). If so, isotope signals in precipitation can be thought to give the same input signal for areas of several hundred square kilometres such as the Blautopf Catchment. Water stable isotopes can therefore help to narrow down the hydrodynamic parameters of the total karstic-fissured-porous system. Specifically, $^{18}O/^{16}O$ and/or D/H ratios are suitable tools because they are constituents of water molecules and thus act as ubiquitous conservative tracers (MALOSZEWSKI et al., 2002).

In this study the main focus was the investigation of diffuse recharge and transport processes in a typical karst system at the catchment scale through a case study of the Blautopf

Catchment. The objective was to investigate the mixing behaviour of the entire system rather than to focus on the fast flow paths of the infiltrated water. This was approached by comparison between the isotopic composition of precipitation and discharge and allowed to decide if mixing occurs in such a fast responsive system or if precipitation reaches the spring unaltered. Furthermore, with caves being present in a well-developed unsaturated zone of up to 150 m thickness, it was possible to investigate to which degree mixing of the water takes place in the unsaturated zone and the epikarst.

The setting of the Blautopf Catchment with its caves enabled convenient sampling of the unsaturated and saturated zones and therefore was ideal to provide new insights into the linkage of these compartments. Such case studies may also help to evaluate the risk of groundwater contamination by diffuse pollution and can provide important insights into water balances.

## 9.2 Materials and Methods

### 9.2.1 Sampling Sites

**General information:** The Blautopf Catchment is situated on the “Schwäbische Alb”, which together with the “Fränkische Alb” makes up the largest karst area in Germany (VILLINGER, 1997). The catchment area is rural and has a size of 165 km$^2$ of which ~ 31 % is covered by forests while more than 60 % is agricultural land (KÖBERLE, 2005).

The Blautopf Catchment has more than 50 caves. Three of them have been chosen for our investigation. They are called “Laichinger Tiefenhöhle” (LTH; 9°41’36’’ E, 48°28’43’’ N), the “Sontheimer Höhle” (SH 9°40’52’’ E, 48°25’52’’ N) that are publicly accessible and the “Hawaii-Schacht” (HWS; 9°41’02’’ E, 48°27’29’’ N) that is not accessible to the general public. The depths below surface were -33 m for LTH, -45 m for SH and -8 m for HWS. While HWS is situated in a dry valley, the entrance of SH is situated in a hill slope and the LTH is located beneath a plain.

The "Schwäbische Alb" has a typical continental climate with an annual average temperature of 6.5 °C (1961 to 1990) (MÜLLER-WESTERMEIER et al., 1999). The average precipitation in the Blautopf Catchment is higher in the northwestern part with 1100 mm a$^{-1}$ and decreases towards the southeastern part to average values of 800 mm a$^{-1}$ (KELLER, 2003) while the mean groundwater recharge in the Blautopf Catchment is about 500 mm a$^{-1}$ (ARMBRUSTER, 2002).

On average the soil cover is about 50 cm and the main soil type is a rendzic leptosol. Underneath this soil cover the thickness of the vadose zone varies between 100 and 150 m.

The thickness of the saturated zone was not determined precisely in this study, but is estimated to range between 50 and 120 m. A comprehensive overview of the hydrology of the Blautopf Catchment is described in VILLINGER (1978). Upstream of the Blautopf Spring, a large cave system with phreatic and vadose zones has been explored up to a length of about 4 km from the spring (www.blautopf.org).

**Geological and hydrogeological settings:** The Blautopf Catchment is situated in the Upper White Jurassic Formation, which mainly consists of limestones and marls. The layers dip southeast. Few tectonic structures are present and have only low displacements (Fig. 9.1). The catchment has two main karst aquifers: The upper one is situated between the "Untere Felsenkalk-Formation" and the "Hangende Bankkalk-Formation". In cases where the limestone is massive, it is differentiated between "Untere" and "Obere Massenkalk-Formation". The basement of these karst aquifers is the "Impressamergel".

The mean discharge of the Blautopf Spring --the principal outlet of the system-- was determined to be 2.43 $m^3$ $s^{-1}$ between 1980 and 2003. However, it shows considerable variability with the highest discharge close to 32 $m^3$ $s^{-1}$ and the lowest of 0.3 $m^3$ $s^{-1}$. This variation is typical for a karst spring and indicates a strong karstification of large parts of the aquifer. According to SELG et al. (2006), rain events and snowmelts can be partially detected in the groundwater recharge of the Blautopf within a short retardation time of 1-2 days, while the mean transit time of the groundwater is around 13 years (BAUER and SELG, 2006).

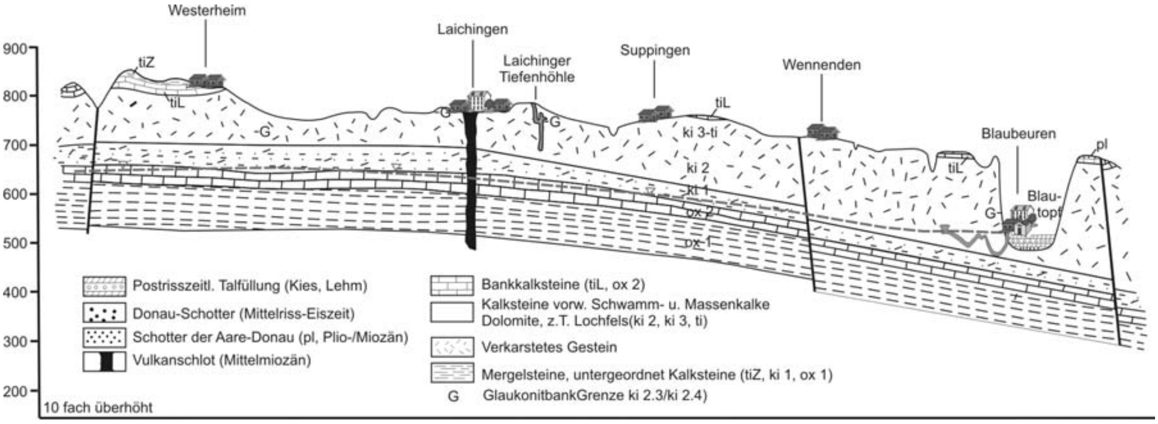

**FIGURE 9.1:** Profile section through the Blautopf Catchment from NW to SE (changed according to VILLINGER, 1987).

### 9.2.2 Stable Isotope Sampling and Analyses

Samples for stable isotope analyses were collected in the caves and the Blautopf Spring between February 2005 and July 2006. In the same time period precipitation was collected with the aim to sample the most representative precipitation events of this period including long term snowfall and thunderstorms. A commercially available rain collector that prevented evaporative loss was placed at the village of Heroldstatt (9°40’01’’ E, 48°26’39’’ N; altitude ~780 m above sea level). After each sampling event, samples were transferred into 20 mL vials with tight screw caps to avoid secondary evaporation effects. Afterwards they were stored upside down at 4 °C in the dark.

The cave seepage waters were collected at three different locations HWS, LTH and SH. In the LTH further three sampling locations with different distances to the surface were chosen to investigate a variety of possible flow paths and residence times. They are the “Vesperhalle” (VH), “Nasser Schacht” (NS) and “Sächsische Schweiz” (TK). Exact locations of these sampling sites are displayed in Fig. 9.2 and range between about -33 and -35 m below the surface. The seepage water was collected with a vial, the filling time of which took several minutes in winter and up to half an hour in summer. The discharge water was collected in the Blautopf Spring from a depth of 20 cm below the surface and a few meters before the outflow. At this location a constant flow ensured supply of freshly discharged water. Samples were taken in the LTH on a regular basis and during events such as snow melts or thunderstorms samples were taken more frequently. Samples from the two other caves were only sampled for general comparison. The main intention was to cover various seasons and to obtain isotope values of marked events such as heavy rain or snow melts. Note that more frequent sampling was often not possible due to safety considerations and limited access to the caves.

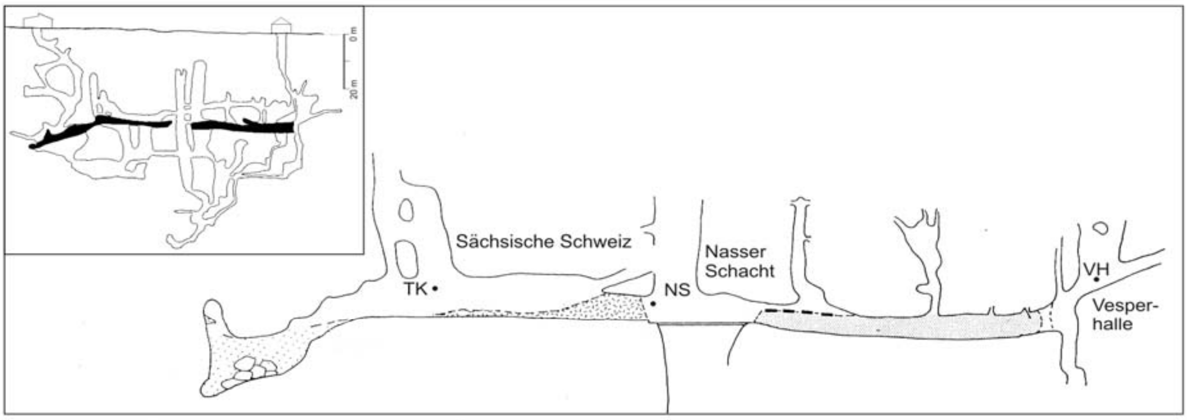

**FIGURE 9.2:** Position profile of the sampling sites in the "Laichinger Tiefenhöhle", TK: "Sächsische Schweiz", NS: "Nasser Schacht" and VH: "Vesperhalle" (changed according to BURGER et al., 1993).

### 9.2.3 Analyses

Stable isotopes ratios of the water were measured at the department for Geochemistry at the Centre for Applied Geosciences (ZAG). A Thermo-Finnigan isotope ratio mass spectrometer (IRMS, Model MAT 252) was used to determine the $^{18}O/^{16}O$ and D/H ratios after equilibration with $CO_2$ and by reduction to $H_2$ gas, respectively. Both parameters were calculated with respect to the international standard VSMOW (Vienna Standard Mean Ocean Water) using the following equation:

$$\delta_{\text{sample}} = \left[ \frac{R_{\text{sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}} \right] \cdot 1000 \qquad [9\text{-}1]$$

where R is the ratio $^{18}O/^{16}O$ or D/H. The one $\sigma$ standard deviation for repeat measurements was ± 0.2 ‰ for $\delta^{18}O$ and ± 1 for $\delta D$. The weighted mean isotopic composition for the precipitation was calculated with:

$$\overline{C_w} = \frac{\sum Q_t C_t}{\sum Q_t} \qquad [9\text{-}2]$$

where $Q_t$ is the rain amount [L $m^{-2}$] and $C_t$ the $\delta^{18}O$ signal of the precipitation water at time t.

### 9.2.4 Climatic Data

Data for precipitation were provided by the sewage plant in Heroldstatt (9°40’42’’ E, 48°26’30’’ N) that has an altitude of 728 m above sea level and is located 0.6 km away from the precipitation sampling station for isotopes. A Hellmann apparatus was used to determine the precipitation amounts. It was emptied every morning and the maximum and minimum temperatures were also recorded each day. The amount of snow was established by melting.

The discharge at the Blautopf Spring was continuously recorded by the "Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg" (Karlsruhe).

## 9.3 Results

Fifty-seven samples were measured for $^{18}O/^{16}O$ ratios in precipitation, 26 for the spring and a sum of 132 for all cave seepage waters. They are listed in appendix F together with sampling dates. For some selected samples the hydrogen isotope values ($\delta D$) were measured and allowed to establish a local meteoric water line.

### 9.3.1 Input of the Isotope Signal

Fig. 9.3 shows the isotopic variability of the precipitation. The $\delta^{18}O$ values reveal clear seasonality patterns with maximum values in summer (-2.9 ‰) and minimum values in winter

(-24.6 ‰). The $\delta^{18}O$ values were also weighted by cumulative precipitation amounts between sampling events and yielded a value of –9.3 ‰ for the period from March 2005 to May 2006. For comparison, BAUER and SELG (2006) determined a weighted mean average of $\delta^{18}O$ of -9.5 ‰ at the station "Münsingen" that is at a distance of 15 Km from Heroldstatt. With lateral distribution patterns of $\delta^{18}O$ in the catchment being relatively homogeneous and assuming negligible altitude effects, few such sampling points can be used to represent the isotopic input for the entire catchment.

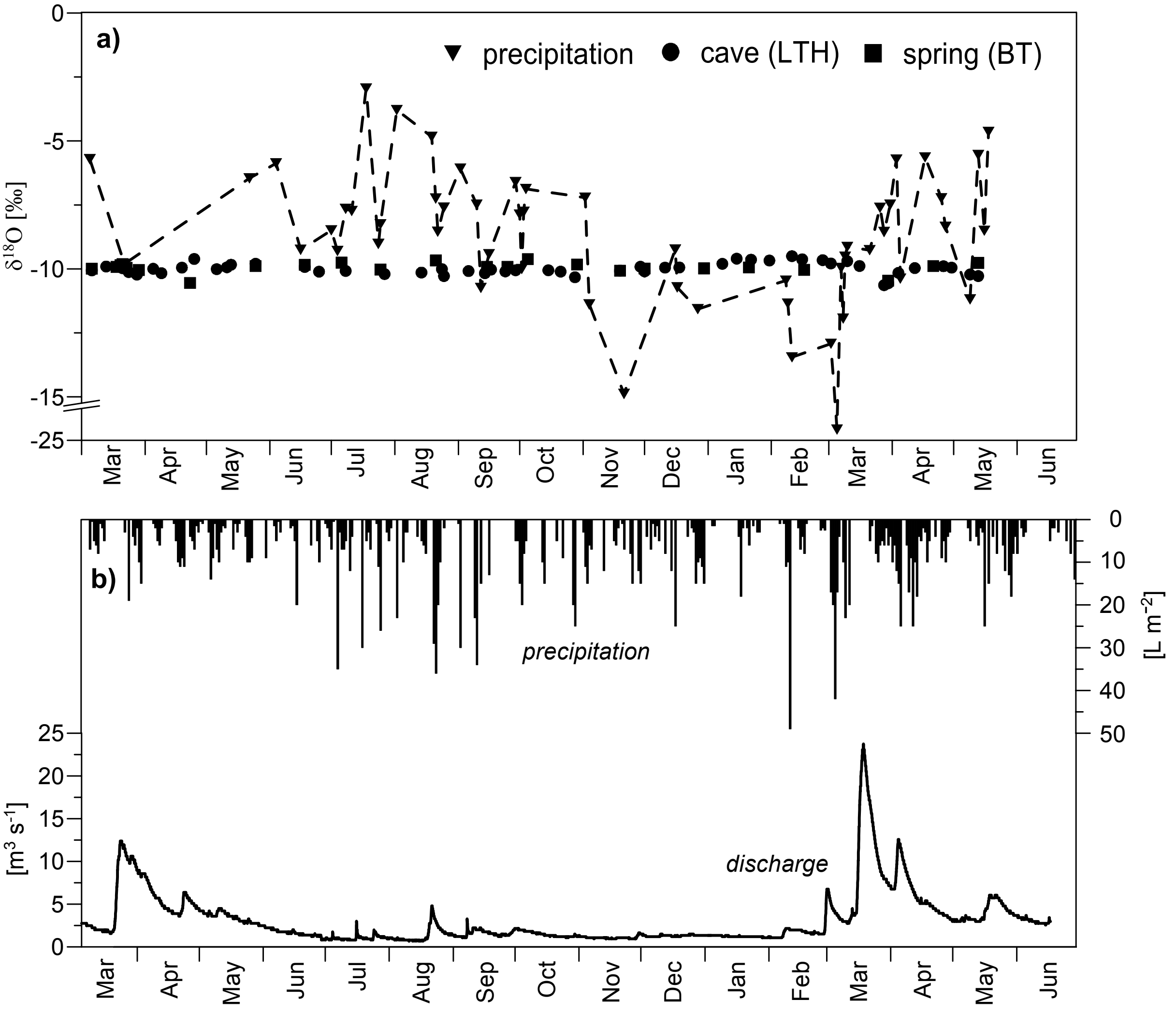

**FIGURE 9.3:** a) $\delta^{18}O$ composition of the rainfall (Heroldstatt), the spring (Blautopf) and the seepage water ("Laichinger Tiefenhöhle") and b) precipitation and the discharge amounts.

## 9.3.2 Isotope Signal of the Seepage and Spring Water

The samples of the seepage and the spring water only varied in a narrow range. They showed oxygen isotope values between -9.5 and -10.6 ‰ for LTH (Fig. 9.4) while the other locations in the caves showed very similar results with $\delta^{18}O$ values ranging from -9.3 to -10.5 ‰, -9.2 to -10.6 ‰, -9.4 to -9.9 ‰ and -9.5 to -10.6 ‰ for VH, NS, TK and HWS, respectively. Location NS is known for a fast response to strong precipitation events; however, even at this subsurface location no significant seasonality in the $\delta^{18}O$ signal was found. For comparison, NORDHOFF (2005) measured $\delta^{18}O$ values in the "Zaininger Höhle" that is also located in the Blautopf Catchment and found similar $\delta^{18}O$ values in the drip water (-10.5 to -11.2 ‰).

With their isotope values ranging around –10 ‰, the cave drip and the Blautopf Spring waters were slightly more negative than the weighted average of the precipitation. This can be explained by the fact that the amount of soil and groundwater recharge during winter was to a lesser extent reduced by evapotranspirative processes when compared to summer recharge. This means that more water with more negative isotope signals recharged during the cold season. The result is a drift towards slightly more negative values of water in the subsurface and the Blautopf Spring. Nonetheless, the differences between Blautopf discharge and weighted recharge are too small to establish a proper mass balance to weigh summer versus winter precipitation.

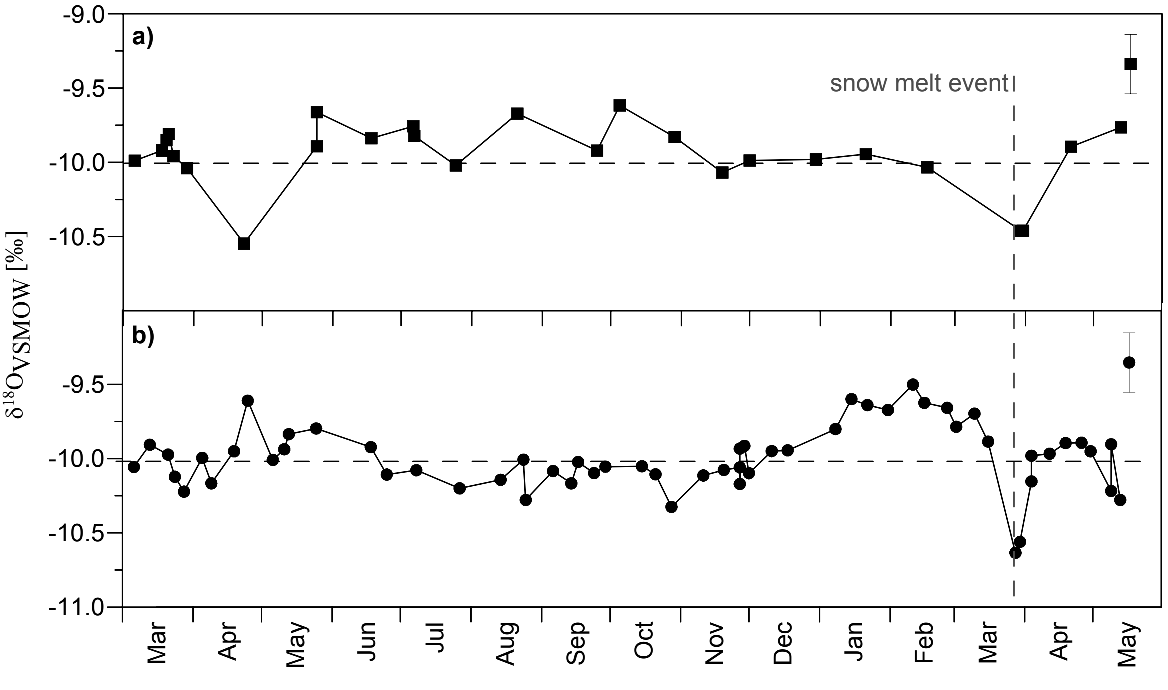

**FIGURE 9.4:** Graph a) shows a detailed $\delta^{18}O$ composition of the Blautopf Spring. The lower graph b) shows the isotopic signal in the "Laichinger Tiefenhöhle". The standard deviation of the $\delta^{18}O$ measurements is indicated in top right.

### 9.3.3 Local Meteoric Water Line

The hydrogen isotope composition (δD) ranged between -68 and -73 ‰ for the LTH and -67 and -72 ‰ for the Blautopf while the precipitation varied between -15 and -125 ‰. Plotting the $\delta^{18}O$ versus δD values of the precipitation yields a linear relationship for the Blautopf Catchment that is known as the local meteoric water line (Fig. 9.5). The isotopic values of cave seepage and Blautopf discharge samples all fell on this line and only small variations in the isotope values of the Blautopf samples were found. If they were influenced by evaporation prior to recharge or from the open surface of the Blautopf, they would follow the typical evaporation trend that is marked as a dashed arrow in figure 4. Since this is not the case, the local precipitation must indeed be responsible for the recharge of the Blautopf Spring with negligible alteration of the isotope signal.

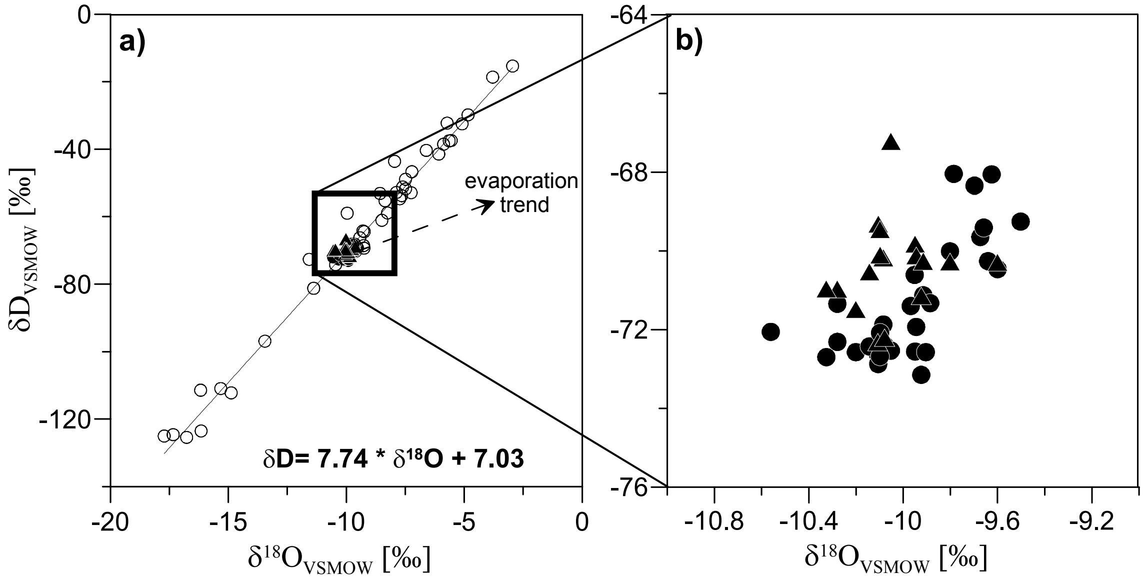

**FIGURE 9.5:** a) Local meteoric water line of the Blautopf Catchment with evaporation trend b) Seepage and ground water in detail. Symbols: ○ rainfall ● seepage water ▲ groundwater.

## 9.4 Discussion

The similarity between cave seepage waters indicates that a significant homogenisation of the water must occur in the upper unsaturated zone regardless of the length of flow path. For instance, even the sampling location HWS, which is only 8 m beneath the surface, shows such buffering. This is further confirmed by the similarity between spring discharge and cave seepage waters. In addition the latter value is very close to the weighted mean $\delta^{18}O$ value of the precipitation. The assumed mechanism to mask the annual isotopic variation of the precipitation is considerable mixing of recharge already in the unsaturated zone. Even heavy rain events during summer only produced slight isotopic increases in the drip water of caves. This conforms to other findings of CABALLERO et al. (1996) who also collected water from wells to show influences of an aquifer system in Nerja in southern Spain and by PERRIN et al. (2003) who sampled spring water from an about 500 m long karstic network near Basel in Switzerland. Both studies demonstrate similarity between recharge and discharge and mixing. Other studies by FULLER et al. (2008) also show buffering of the recharge water by comparing isotope analyses of cave drip waters and local precipitation.

If such homogenisation takes place in the epikarst, interactions of slow water movement and storage are plausible mechanisms. While base flow preferentially enables gravimetric movement of more easily mobilised water in fast conduit systems, heavy rain events can also flood and subsequently connect smaller fissures. In such a case, the hydraulic pressure can mobilise pre-event water out of the storage zone towards the larger conduits in a piston flow effect. This concept can explain mixing in the seepage water while the main function of the fast conduit system remains transport of the already mixed water. CRUZ Jr. et al. (2005) stated that karst seepage flow is largely influenced by storage capacity. They also found that the drip discharge is often delayed in time depending on thickness and character of the unsaturated zone. This supports the assumption that the main mixing and storage processes occur in the upper part of the unsaturated zone. Hydrochemical and isotope studies from various regions, for instance from the Arabika Massif in New Zealand and from New Mexico, demonstrate that a delay in flow caused by storage in the epikarst can range from several days to a few months (KLIMCHOUK and JABLOKOVA, 1989; WILLIAMS, 1983). On the other hand, seasonal variations of $\delta^{18}O$ were found to be significantly reduced after about 3.5 years of residence time in the soil and epikarst zone in the neighboring "Fränkische Alb" (STICHLER and HERRMANN, 1983). With the current data set it is not possible to determine exact travel times of water. Nonetheless, the above research findings provide the boundary conditions for residence times of water in the unsaturated zone. EINSIEDL (2005) and EINSIEDL & MAYER (2005) established that the fissured-porous aquifer, especially the rock matrix, is the main water storage, whereas the soil and the epikarst only have a low storage capacity. Nonetheless, the rock matrix in the Blautopf Catchment, especially in the environment of the "Laichinger Tiefenhöhle" consists of the "Lochfelsfazies" with a high porosity. PERRIN et al. (2003) also stipulated that the soil and the epikarst subsystems appear to act as an important storage element. However, with the current data set, a differentiation between these compartments is not possible. In any case, the homogenisation of the isotopic composition seems to take place close to the surface. This is confirmed by other workers who found a good match between the isotopic composition of drip and the soil waters in Brazil (CRUZ Jr et al., 2005).

The good agreement in isotope numbers between cave seepage and Blautopf discharge also implies that only a minor part of heavy precipitation events bypasses the epikarst and soil zone in preferential flow paths. This is confirmed by the fact that even high discharge seems to provoke only a slight change of the isotopic composition in the Blautopf Spring. The proposition that only a small part of the precipitation reaches the discharge directly was also confirmed with modeling where the conductive part of the complete discharge was determined to be only about 1 % even though during extreme events the fast conduit discharge can reach 5 to 10 % of the total flow (BAUER and SELG, 2006).

The possibility of a connection with adjacent basins could also be tested, particularly if cave systems spread beyond the surface area of the catchment. Since all isotope data presented of the Blautopf case study lie on the meteoric water line, we can assume that the Blautopf Spring has been fed by local recharge. Alternatively, if caves extend to adjacent catchments, they have received recharge of similar isotopic composition.

A calculation of proportions such as summer recharge to winter discharge was not possible as this requires output isotopic compositions that arrive with a time delay to the input. However, this could not be found since the isotope signal is already too buffered in the cave. Therefore, the given results do not enable quantification of mixing proportions as the weighted average of precipitation, cave seepage, and groundwater discharge through the Blautopf Spring are too similar.

An investigation of persistent pollutants in the same area produced findings that match the isotope investigation presented here. It showed that the largest amounts of POPs reached the saturated zone shortly after high discharge events such as snow melts. This can be explained by the piston flow effect that mobilizes particles deposited in the fissures of the epikarst with increasing pressures resulting from higher precipitation amounts. After the fissures are flooded and connected the infiltrated water is able to transport the particles towards the receiving stream. The Blautopf Spring reacts very fast to snow melts and heavy rain events, thus confirming it to have a saturated conduit system (BIRK et al., 2004).

It is also interesting to compare the above results to the nearby "Gallus Quelle" where the $\delta^{18}O$ signal of the discharge decreased with smaller amounts (SAUTER, 1992). The explanation for such a trend is the mobilization of old winter recharge that was stored in lower aquifer zones and only released from storage during low-flow conditions. Such tendencies could not be observed in the Blautopf Spring. An explanation for this discrepancy could be that with an average of 0.5 $m^3$ $s^{-1}$ the discharge amount from the "Gallus Quelle" is much less than the Blautopf discharge with average of about 2.4 $m^3$ $s^{-1}$. With this the Blautopf cave system establishes a comparatively larger mixing pool where such delay effects might be masked. Further studies on the Gallus Quelle showed that its spring hydrograph does not reveal temporal recharge distributions (GEYER et al., 2008). This supports the isotope results on the Blautopf Catchment although the work presented here rather focuses on mixing in the unsaturated zone directly after the recharge.

## 9.5 Summary

By investigating the karst aquifer of the Blautopf Catchment with water stable isotopes the following conclusions could be drawn:

- The variations of the stable isotope signal of the precipitation was not found in the Blautopf discharge, which was homogeneous throughout the year. This indicates that considerable mixing must take place in the subsurface of the catchment. It also confirms that fast conduit systems play a minor role in the water balance.
- The stable isotope signal of the precipitation was already buffered in the vadose zone and the cave seepage water only showed minor variations in its isotopic composition that was very similar to the isotope value of the Blautopf Spring (i.e. groundwater) and the weighted averages of the annual precipitation. This is in contrast to the isotope curve of the precipitation and indicates a considerable mixing in the unsaturated zone.
- At present it is difficult to decide which compartment in the unsaturated zone is most responsible for mixing the incoming water masses, however the most likely candidates are the soil and epikarst compartments.

The mixing of water seemed to be maintained even during high discharge (e.g. after snow melts). This is shown by the Blautopf Spring always ranging around its homogeneous isotope values of –10 ‰. Nonetheless, other investigations showed increased mobilisation of pollutants during such times. This may be explained through involvement of the fine fracture system of the epikarst that may hold back and release pollutants over several years.

Future work should focus on investigations of the buffer capacity of the soil and epikarst zone and more research should be devoted to the bedrock matrix. Further dynamic tracers such as tritium isotopes could reveal better insight into travel times of subsurface water masses, while higher sample frequencies may be able to resolve quantification of events such as snow melts and heavy precipitation and the role of the fast conduit system.

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# CHAPTER 10

# SUMMARY AND CONCLUSIONS

The aim of this work was to find to determine a input/output mass balance for PAHs in a karst system. Within this, the appearances of break throughs of contaminants have been investigated in this area. For these purposes a two year monitoring program was executed. This program included different parameters: the atmospheric deposition supplied the input into the catchment area; the soil showed accumulation processes; the seepage and groundwater delivered insight into transport activities in the karst aquifer. Furthermore, the monitoring of the spring enabled to determine the output of the whole system. With these data sets it was possible to establish an input/output mass balance for the studied area.

This approach yielded the main result, that there is actual no risk for the groundwater concerning PAHs in the study area. Because more than 80 % of PAHs stay in the system and get not released. However, there were significant break throughs during high flow events in the seepage, as well as in the groundwater at the spring.

The bulk atmospheric deposition rates into the Blautopf Catchment showed a seasonal cycle with higher values during winter. The mean annual deposition rates were very consistent for all locations, they varied in the range of 187-254 ng $d^{-1}$ $m^{-2}$ (1. year) and 152-195 ng $d^{-1}$ $m^{-2}$ (2. year) (without settlement). Thus, it was possible to use the input data to calculate the mass balance for the whole area. During winter the highest deposition rate was found in the village (1983 ng $d^{-1}$ $m^{-2}$). This result shows directly the effect of domestic space heating during the cold season. This means for the mass balance to use higher values for towns. The distribution pattern of PAHs showed clearly that the input of PAHs was mainly delivered in association with particles.

Soils are an important factor controlling the storage, fate and transport of PAHs. The main established result in this investigation was that PAHs accumulate in the top soils of the Blautopf Catchment. Concentrations of the soils are partly fairly high; this gives evidence of the good storage capacity of the soils, especially of the top soils. The sorption is mainly based on partitioning processes. The distribution patterns of the soils and the atmospheric deposition are almost equal, that means the atmosphere is the main supplier of PAHs to the soils. In the loamy sediments of the caves almost no PAHs were found. This indicates that there are no significant transport processes into deeper parts of the Blautopf Catchment.

The investigation of the seepage water showed that the German limit for drinking water was clearly exceeded in two caves. Normally, the concentrations of PAHs were very low, but during high discharge events, like snowmelts, they increased obviously (hundredfold). This shows that there is a risk of the groundwater during high flow events. However these events are temporary and occur not so often during a circle of the year (heavy rain events, snow melts, etc.). During normal flow conditions the concentrations stayed far below the limit. By means of the distribution patterns it was possible to assert that transport processes mainly take place in association with particles. The dissolved percentage of PAHs is not important for transport processes in the study area.

The background concentration of PAHs in the Blautopf Spring is around 10 ng $L^{-1}$. During "normal" flow conditions this value is fairly stable. However, during high flow events, such as snow melts, the concentrations of PAHs can increase dramatically. This increase can be correlated with a higher discharge and turbidity. But within this finding there are also high turbidity events with no higher concentration of PAHs. Thus, further investigation should be done. The German limit for drinking water for BaP was clearly exceeded during the snow melt of 2006, when the discharge was higher than 26 $m^3$ $s^{-1}$. It is necessary to use the two different sampling methods, because events can only be sampled by the established sampling with bottles. The time integrated sampler can not resolve short events with higher concentrations (snowmelts, etc.). It gives good results for a long time monitoring, whereas only the background information is important. The sampling devices were concluded to supply good and stable results and were considered to be easy to handle and relatively inexpensive. It has also been concluded that the main transport mechanism of PAHs can be associated with particles. It could not be clarified if the particles came directly from the surface or if they had been re-suspended.

The field site investigation provided a methodology with which it was possible to follow the pollutants from the atmosphere into the groundwater and establish a input/output mass balance in the Blautopf Catchment. The main result is, that about 90 % of PAHs do not reach the groundwater and accumulate in top soils. Furthermore, ca. 50 % of all output of PAHs is associated with events like snowmelts and high flow. The input into and the transport through the karst system is dominated by particle associated PAHs. Particulate transport was the main process to move PAHs from the surface to the spring. This was proved by a correlation of distribution patterns from the different compartments (atmosphere, seepage and groundwater). However, it could not be determined if the particles were re-suspended or directly delivered from the surface along preferential flow paths. A pressure pulse mechanism (e.g. piston flow effect) is the main factors controlling the mobilisation of particles, because they only appear in connection with higher flow rates. This means that the stored water in the soil, epikarst and unsaturated zone was pushed downwards and the new infiltrated water displaced the older one. Subsequent the unsaturated fissures in the rock matrix were flooded and connected, within this the flow rate increased. Especially the epikarst was probably the main supplier to these pathways. However, part of the new infiltrating water bypassed the storage zones along preferential flow paths. Finally, the system started to empty the fissures, so they lost their connection to each other and the concentrations decreased again.

To prove the findings from the input/output mass balance oxygen stable isotopes were investigated. The variability of the stable isotope signal of the precipitation was not found in the Blautopf discharge, which was homogeneous throughout the year. This indicates that considerable mixing must take place in the subsurface of the catchment. It also confirms that fast conduit systems play a minor role in the water balance. The stable isotope signal of the precipitation was already buffered in the vadose zone and the cave seepage water did only show little variability in its isotopic composition that was very similar to the isotope value of the Blautopf Spring (i.e. groundwater) and the weighted averages of the annual precipitation. At present it is difficult to decide which compartment in the unsaturated zone is most responsible for mixing the incoming water masses but the most likely candidates are the soil and epikarst compartments. The mixing of water seemed to be maintained even during high discharge (e.g. after snowmelts) because the Blautopf Spring always maintained its homogeneous isotope values. Nonetheless, other investigations showed increased mobilisation of pollutants during such times. This may be explained through involvement of the fine fracture system of the epikarst.

The complexity of the processes in a karst aquifer makes it difficult to predict the fate and transport of pollutants. This work indicates that there is a large pollutants storage capacity, because the most part of the input via atmosphere does not reach the output.

# APPENDIX

**Table A-1:** Atmospheric deposition rates [ng $d^{-1}$ $m^{-2}$] in the Blautopf Catchment from June 2004 till July 2006.

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GH+SL blank** | | | | | | | | | | | | | | | | | | |
| 22.06.-27.08.04 | 0 | 6 | 7 | 18 | 1 | 3 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 36 |
| 27.08.-24.12.04 | 3 | 12 | 4 | 18 | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 42 |
| 24.12.04-19.03.05 | 3 | 1 | 3 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| 19.03.-16.05.05 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| 16.05.-19.07.05 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| 19.07.-14.09.05 | 1 | 1 | 1 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 14.09.-13.11.05 | 1 | 1 | 2 | 6 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13 |
| 13.11.05-16.01.06 | 2 | 2 | 3 | 7 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 19 |
| 16.01.-10.03.06 | 1 | 1 | 1 | 3 | 0 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 11 |
| 10.03.-13.05.06 | 3 | 4 | 3 | 7 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 21 |
| 13.05.-19.07.06 | 1 | 0 | 1 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 |
| **GH BS** | | | | | | | | | | | | | | | | | | |
| 22.06- 27.08.04 | 5 | 4 | 7 | 52 | 3 | 71 | 57 | 21 | 25 | 29 | 12 | 17 | 15 | 2 | 27 | 4 | 20 | 372 |
| 27.08.-19.12.05 | 12 | 5 | 9 | 70 | 4 | 39 | 29 | 8 | 15 | 18 | 8 | 10 | 8 | 2 | 15 | 4 | 13 | 268 |
| 19.12.04-25.02.05 | 10 | 2 | 15 | 175 | 10 | 193 | 139 | 57 | 101 | 103 | 44 | 54 | 42 | 10 | 72 | 10 | 56 | 1094 |
| 25.02.-19.03.05 | 23 | 4 | 60 | 406 | 22 | 422 | 308 | 83 | 141 | 132 | 56 | 68 | 54 | 10 | 101 | 15 | 79 | 1983 |
| 19.03.-16.05.05 | 16 | 1 | 11 | 130 | 7 | 84 | 62 | 24 | 37 | 48 | 21 | 29 | 23 | 7 | 39 | 7 | 34 | 579 |
| 16.05.-19.07.05 | 6 | 1 | 5 | 44 | 4 | 42 | 31 | 12 | 20 | 18 | 8 | 11 | 10 | 2 | 15 | 0 | 15 | 245 |
| 19.07.-14.09.05 | 6 | 2 | 7 | 44 | 2 | 43 | 31 | 14 | 21 | 27 | 12 | 17 | 14 | 2 | 24 | 4 | 22 | 292 |
| 14.09.-12.11.05 | 8 | 2 | 7 | 40 | 3 | 39 | 29 | 10 | 18 | 25 | 11 | 14 | 11 | 0 | 16 | 2 | 15 | 250 |
| 12.11.05-15.01.06 | 17 | 3 | 19 | 137 | 6 | 99 | 59 | 13 | 27 | 33 | 14 | 18 | 14 | 2 | 20 | 3 | 19 | 501 |
| 15.01.-10.03.06 | 39 | 4 | 20 | 236 | 15 | 258 | 186 | 51 | 101 | 83 | 36 | 42 | 31 | 5 | 51 | 8 | 44 | 1211 |

**Table A-1:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10.03.-13.05.06 | 20 | 4 | 14 | 112 | 7 | 95 | 65 | 19 | 40 | 41 | 18 | 23 | 19 | 3 | 24 | 5 | 24 | 531 |
| 13.05.-19.07.06 | 13 | 2 | 4 | 33 | 3 | 35 | 24 | 6 | 13 | 13 | 5 | 8 | 6 | 1 | 7 | 1 | 8 | 181 |
| **GH SH** | | | | | | | | | | | | | | | | | | |
| 22.06.-27.08.04 | 2 | 3 | 5 | 21 | 1 | 13 | 9 | 3 | 5 | 6 | 3 | 4 | 4 | 1 | 5 | 1 | 4 | 89 |
| 27.08.-24.12.04 | 3 | 5 | 6 | 48 | 2 | 21 | 15 | 4 | 10 | 13 | 6 | 6 | 5 | 1 | 11 | 3 | 10 | 168 |
| 24.12.04-18.03.05 | 2 | 3 | 10 | 71 | 4 | 93 | 40 | 7 | 20 | 18 | 8 | 10 | 8 | 1 | 18 | 2 | 13 | 328 |
| 18.03.-16.05.05 | 2 | 1 | 4 | 65 | 2 | 26 | 18 | 6 | 13 | 18 | 8 | 10 | 8 | 2 | 15 | 4 | 13 | 216 |
| 16.05.-19.07.05 | 0 | 0 | 2 | 11 | 0 | 10 | 7 | 4 | 6 | 5 | 2 | 4 | 3 | 0 | 0 | 0 | 3 | 78 |
| 19.07.-14.09.05 | 1 | 1 | 3 | 17 | 1 | 19 | 15 | 7 | 11 | 16 | 7 | 10 | 9 | 1 | 13 | 2 | 12 | 899 |
| 14.09.-12.11.05 | 3 | 2 | 4 | 22 | 1 | 14 | 10 | 4 | 5 | 8 | 3 | 4 | 4 | 1 | 4 | 1 | 5 | 436 |
| 12.11.05-16.01.06 | 3 | 2 | 5 | 22 | 1 | 12 | 6 | 2 | 3 | 4 | 2 | 2 | 2 | 0 | 2 | 0 | 2 | 167 |
| 16.01.-10.03.06 | 4 | 3 | 12 | 313 | 2 | 34 | 17 | 5 | 12 | 11 | 5 | 5 | 4 | 1 | 8 | 1 | 7 | 516 |
| 10.03.-13.05.06 | 5 | 2 | 7 | 57 | 3 | 44 | 28 | 8 | 20 | 21 | 9 | 12 | 9 | 1 | 12 | 3 | 12 | 317 |
| 13.05.-19.07.06 | 12 | 2 | 2 | 22 | 2 | 26 | 18 | 3 | 7 | 7 | 3 | 5 | 4 | 1 | 4 | 1 | 4 | 158 |
| **GH SoS** | | | | | | | | | | | | | | | | | | |
| 22.06.-27.08.04 | 3 | 5 | 6 | 30 | 1 | 21 | 13 | 5 | 7 | 8 | 3 | 5 | 5 | 0 | 8 | 1 | 6 | 128 |
| 27.08.-24.12.04 | 5 | 0 | 8 | 61 | 11 | 53 | 72 | 17 | 23 | 27 | 12 | 14 | 15 | 3 | 26 | 14 | 24 | 385 |
| 24.12.04-18.03.05 | 4 | 5 | 8 | 58 | 4 | 73 | 30 | 5 | 13 | 12 | 5 | 6 | 4 | 0 | 13 | 2 | 8 | 249 |
| 18.03.-16.05.04 | 4 | 1 | 5 | 41 | 3 | 32 | 22 | 11 | 17 | 22 | 9 | 13 | 11 | 3 | 19 | 3 | 20 | 235 |
| 16.05.-19.07.05 | 0 | 0 | 4 | 17 | 0 | 17 | 11 | 5 | 9 | 8 | 4 | 5 | 5 | 1 | 6 | 1 | 6 | 98 |
| 19.07.-14.09.05 | 3 | 3 | 6 | 30 | 1 | 27 | 20 | 8 | 14 | 20 | 9 | 13 | 11 | 2 | 18 | 3 | 16 | 203 |
| 14.09.-12.11.05 | 3 | 2 | 5 | 25 | 1 | 24 | 18 | 6 | 11 | 16 | 7 | 9 | 8 | 0 | 10 | 2 | 10 | 157 |

**Table A-1:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12.11.05-16.01.06 | 4 | 2 | 7 | 33 | 1 | 21 | 12 | 3 | 8 | 9 | 4 | 5 | 4 | 1 | 6 | 1 | 6 | 127 |
| 16.01.-10.03.06 | 7 | 3 | 11 | 160 | 3 | 59 | 32 | 7 | 22 | 19 | 8 | 10 | 6 | 1 | 13 | 2 | 12 | 374 |
| 10.03.-13.05.06 | 7 | 3 | 6 | 42 | 3 | 40 | 26 | 8 | 20 | 21 | 9 | 12 | 10 | 2 | 13 | 3 | 14 | 237 |
| 13.05.-19.07.06 | 3 | 1 | 3 | 19 | 1 | 19 | 13 | 4 | 9 | 10 | 4 | 6 | 5 | 1 | 6 | 1 | 6 | 113 |
| **GH HWS** | | | | | | | | | | | | | | | | | | |
| 22.06.-27.08.04 | 4 | 7 | 8 | 38 | 2 | 27 | 15 | 5 | 8 | 9 | 4 | 5 | 5 | 1 | 9 | 2 | 7 | 155 |
| 27.08.-24.12.04 | 3 | 5 | 6 | 51 | 2 | 26 | 19 | 5 | 11 | 15 | 6 | 7 | 6 | 1 | 13 | 5 | 12 | 192 |
| 24.12.04-17.02.05 | 1 | 3 | 4 | 47 | 3 | 79 | 13 | 3 | 7 | 8 | 3 | 3 | 3 | 0 | 10 | 0 | 7 | 196 |
| 17.02.-19.03.05 | 4 | 11 | 116 | 4 | 59 | 32 | 6 | 18 | 39 | 10 | 4 | 10 | 3 | 36 | 7 | 26 | 26 | 410 |
| 19.03.-16.05.05 | 4 | 0 | 5 | 64 | 2 | 44 | 30 | 15 | 22 | 31 | 13 | 17 | 15 | 4 | 27 | 5 | 22 | 322 |
| 16.05.-19.07.05 | 0 | 1 | 3 | 23 | 1 | 16 | 9 | 5 | 9 | 9 | 4 | 5 | 5 | 0 | 6 | 0 | 5 | 101 |
| 19.07.-14.09.05 | 2 | 2 | 5 | 30 | 1 | 29 | 19 | 9 | 15 | 23 | 10 | 14 | 12 | 2 | 18 | 3 | 14 | 206 |
| 14.09.-13.11.05 | 3 | 2 | 5 | 28 | 2 | 27 | 19 | 5 | 9 | 15 | 6 | 9 | 7 | 0 | 8 | 1 | 8 | 154 |
| 13.11.05-14.01.06 | 4 | 3 | 6 | 28 | 1 | 17 | 9 | 2 | 5 | 5 | 2 | 3 | 2 | 0 | 3 | 1 | 3 | 95 |
| 15.01.-16.02.06 | 8 | 9 | 9 | 57 | 2 | 72 | 14 | 3 | 7 | 7 | 3 | 3 | 3 | 0 | 5 | 0 | 5 | 208 |
| 16.02.-10.03.06 | 3 | 1 | 2 | 18 | 1 | 4 | 4 | 1 | 2 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 40 |
| 17.03.-13.05.06 | 6 | 5 | 11 | 101 | 4 | 48 | 33 | 9 | 20 | 18 | 8 | 10 | 8 | 2 | 13 | 2 | 13 | 309 |
| 13.05.-19.07.06 | 5 | 1 | 2 | 23 | 1 | 20 | 12 | 3 | 7 | 7 | 3 | 4 | 3 | 1 | 4 | 1 | 4 | 101 |
| **SL LTH I** | | | | | | | | | | | | | | | | | | |
| 09.07.-17.09.04 | 6 | 6 | 8 | 49 | 5 | 52 | 38 | 23 | 25 | 33 | 14 | 17 | 21 | 5 | 17 | 5 | 15 | 339 |
| 17.09.-24.12.04 | 6 | 0 | 9 | 57 | 6 | 34 | 53 | 6 | 13 | 17 | 7 | 8 | 9 | 1 | 19 | 9 | 19 | 272 |
| 24.12.04-18.03.05 | 2 | 2 | 11 | 71 | 2 | 48 | 28 | 7 | 20 | 21 | 9 | 12 | 9 | 2 | 18 | 3 | 15 | 281 |

**Table A-1:** Continuation

| | **Any** | **Ace** | **Fln** | **Phe** | **Ant** | **Fth** | **Py** | **BaA** | **Chr** | **BbF** | **BkF** | **BeP** | **BaP** | **Per** | **Indo** | **DahA** | **BghiP** | **∑PAHs** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18.03.-16.05.05 | 3 | 0 | 6 | 80 | 3 | 38 | 26 | 10 | 17 | 24 | 10 | 14 | 11 | 3 | 21 | 4 | 19 | 289 |
| 16.05.-19.07.05 | 1 | 0 | 3 | 23 | 1 | 24 | 19 | 28 | 7 | 14 | 6 | 9 | 7 | 1 | 10 | 2 | 9 | 164 |
| 19.07.-14.09.05 | 3 | 1 | 6 | 34 | 2 | 36 | 25 | 15 | 19 | 26 | 11 | 16 | 13 | 2 | 23 | 4 | 21 | 260 |
| 14.09.-12.11.05 | 2 | 1 | 4 | 20 | 1 | 21 | 16 | 6 | 10 | 16 | 7 | 9 | 8 | 1 | 11 | 2 | 10 | 146 |
| 12.11.05-15.01.06 | 4 | 2 | 8 | 40 | 1 | 23 | 12 | 3 | 6 | 7 | 3 | 4 | 3 | 0 | 4 | 1 | 4 | 124 |
| 14.01.-10.03.06 | 5 | 17 | 15 | 98 | 5 | 58 | 31 | 8 | 25 | 20 | 9 | 9 | 7 | 1 | 1 | 12 | 11 | 331 |
| 10.03.-13.05.06 | 5 | 7 | 9 | 60 | 7 | 53 | 35 | 10 | 18 | 21 | 9 | 12 | 10 | 2 | 17 | 3 | 17 | 297 |
| 13.05.-19.07.06 | 4 | 3 | 6 | 69 | 15 | 120 | 96 | 61 | 52 | 72 | 31 | 41 | 54 | 10 | 38 | 10 | 31 | 712 |
| **SL LTH II** | | | | | | | | | | | | | | | | | | |
| 09.07.-17.09.04 | 4 | 4 | 5 | 35 | 3 | 44 | 31 | 14 | 21 | 27 | 11 | 18 | 16 | 4 | 17 | 4 | 15 | 272 |
| 17.09.-24.12.04 | 5 | 6 | 8 | 59 | 2 | 36 | 27 | 8 | 17 | 21 | 9 | 10 | 10 | 2 | 19 | 4 | 15 | 256 |
| 24.12.04-18.03.05 | 2 | 1 | 9 | 54 | 2 | 30 | 17 | 5 | 12 | 13 | 6 | 8 | 6 | 1 | 11 | 2 | 9 | 189 |
| 18.03.-16.05.05 | 3 | 1 | 6 | 79 | 3 | 49 | 35 | 13 | 22 | 31 | 13 | 18 | 15 | 4 | 28 | 6 | 24 | 350 |
| 16.05.-19.07.05 | 0 | 2 | 5 | 42 | 2 | 32 | 19 | 9 | 15 | 12 | 5 | 8 | 7 | 1 | 10 | 2 | 9 | 181 |
| 19.07.-14.09.05 | 2 | 2 | 7 | 35 | 2 | 33 | 22 | 8 | 18 | 22 | 9 | 14 | 11 | 2 | 17 | 2 | 15 | 221 |
| 14.09.-12.11.05 | 3 | 2 | 5 | 28 | 1 | 24 | 17 | 5 | 9 | 13 | 6 | 7 | 6 | 1 | 8 | 1 | 8 | 144 |
| 12.11.05-15.01.06 | 4 | 3 | 8 | 36 | 1 | 20 | 10 | 3 | 6 | 6 | 3 | 4 | 3 | 0 | 4 | 1 | 4 | 114 |
| 14.01.-10.03.06 | 5 | 1 | 10 | 71 | 3 | 55 | 32 | 9 | 21 | 20 | 9 | 11 | 8 | 1 | 17 | 3 | 18 | 294 |
| 10.03.-13.05.06 | 4 | 2 | 8 | 56 | 3 | 51 | 35 | 11 | 23 | 26 | 11 | 15 | 12 | 2 | 15 | 3 | 15 | 291 |
| 13.05.-19.07.06 | 4 | 2 | 2 | 23 | 1 | 24 | 15 | 4 | 9 | 9 | 4 | 5 | 4 | 1 | 5 | 1 | 5 | 119 |

**Table A-2:** Gas phase sampling [ng d$^{-1}$] in the Blautopf Catchment from July 2005 till July 2006.

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF/ BkF | BeP | BaP | Per | Indo | DahA | BghiP | ΣPAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GH+SL blank** | | | | | | | | | | | | | | | | | |
| 19.07.-14.09.05 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |
| 14.09.-13.11.05 | 0.0 | 0.1 | 0.1 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| 13.11.05-16.01.06 | 0.1 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| 16.01.-10.03.06 | 0.0 | 0.0 | 0.1 | 0.2 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 |
| 10.03.-13.05.06 | 0.1 | 0.2 | 0.2 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 |
| 13.05.-19.07.06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |
| **GH SoS gas** | | | | | | | | | | | | | | | | | |
| 19.70.-14.09.05 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 |
| 14.09.-12.11.05 | 0.0 | 0.1 | 0.1 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| 12.11.05-16.01.06 | 0.1 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| 16.01.-10.03.06 | 0.1 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| 10.03.-13.05.06 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 |
| 13.05.-19.07.06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |
| **GH HWS gas** | | | | | | | | | | | | | | | | | |
| 19.07.-14.09.05 | 0.0 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 |
| 14.09.-13.11.05 | 0.0 | 0.0 | 0.1 | 0.3 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 |
| 13.11.05-14.01.06 | 0.1 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| 14.01.-10.03.06 | 0.0 | 0.0 | 0.1 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| 10.03.-13.05.06 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| 13.05.-19.07.06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |

**Table A-2:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF/ BkF | BeP | BaP | Per | Indo | DahA | BghiP | $\Sigma$PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GH BS gas** | | | | | | | | | | | | | | | | | |
| 19.07.-14.09.05 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |
| 14.09.-12.11.05 | 0.0 | 0.0 | 0.1 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| 12.11.05-16.01.06 | 0.1 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| 15.01.-10.03.06 | 0.0 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 |
| 10.03.-13.05.06 | 0.1 | 0.0 | 0.1 | 0.3 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.8 |
| 13.05.-19.07.06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 |
| **GH SH gas** | | | | | | | | | | | | | | | | | |
| 19.07.-14.09.05 | 0.0 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| 14.09.-12.11.05 | 0.0 | 0.1 | 0.1 | 0.2 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 |
| 12.11.05-16.01.06 | 0.1 | 0.1 | 0.1 | 0.3 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| 16.01.-10.03.06 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 |
| 10.03.-13.05.06 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| 13.05.-19.07.06 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| **SL LTH gas** | | | | | | | | | | | | | | | | | |
| 19.07.-14.09.05 | 0.0 | 0.7 | 0.7 | 5.0 | 0.0 | 1.2 | 0.6 | 0.0 | 0.0 | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 9.1 |
| 14.09.-12.11.05 | 1.0 | 2.1 | 2.9 | 7.1 | 0.2 | 1.1 | 0.7 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 15.9 |
| 12.11.05-15.01.06 | 1.6 | 1.3 | 1.9 | 38.5 | 0.4 | 1.6 | 1.2 | 0.3 | 0.4 | 0.4 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 48.0 |
| 15.01.-10.03.06 | 0.7 | 0.9 | 1.8 | 3.9 | 0.1 | 1.3 | 0.7 | 0.2 | 0.3 | 0.3 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 10.5 |
| 10.03.-13.05.06 | 1.3 | 0.7 | 1.2 | 2.8 | 0.2 | 1.0 | 0.6 | 0.4 | 0.3 | 0.6 | 0.0 | 0.3 | 0.0 | 0.3 | 0.3 | 0.4 | 10.3 |
| 13.05.-19.07.06 | 1.0 | 1.2 | 1.4 | 5.2 | 0.2 | 1.2 | 0.7 | 0.3 | 0.3 | 0.5 | 0.1 | 0.2 | 0.0 | 0.2 | 0.2 | 0.2 | 12.8 |

**Table A-3:** Results from leaf sampling [µg kg$^{-1}$] in the Blautopf Catchment.

| June | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | Σ PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| fir | 0.0 | 0.0 | 1.2 | 5.3 | 0.3 | 2.4 | 1.9 | 0.6 | 1.4 | 1.9 | 0.8 | 0.3 | 0.2 | 0.0 | 0.3 | 0.1 | 0.3 | 16.8 |
| pine | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 |
| maple | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

| October | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | Σ PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| beech | 7.9 | 11.2 | 42.4 | 391.9 | 19.5 | 99.4 | 71.5 | 2.5 | 7.5 | 3.2 | 1.4 | 3.5 | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 | 663.3 |
| basswood | 8.1 | 13.0 | 33.0 | 278.6 | 18.5 | 106.1 | 93.7 | 12.2 | 27.8 | 7.5 | 3.2 | 4.2 | 2.0 | 0.5 | 1.3 | 0.2 | 1.7 | 611.4 |
| fir | 1.2 | 4.6 | 3.7 | 31.2 | 1.7 | 13.1 | 10.6 | 1.5 | 4.4 | 3.2 | 1.4 | 1.6 | 1.0 | 0.1 | 0.9 | 0.1 | 1.3 | 81.5 |
| chestnut | 10.4 | 5.3 | 20.4 | 239.0 | 16.2 | 78.1 | 56.1 | 3.8 | 13.9 | 7.0 | 3.0 | 2.3 | 2.3 | 0.4 | 2.9 | 0.3 | 2.5 | 464.0 |
| aspen | 4.3 | 12.1 | 27.3 | 387.7 | 28.0 | 117.7 | 86.7 | 2.9 | 8.3 | 0.3 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 675.3 |
| apple tree | 8.9 | 12.1 | 63.3 | 292.5 | 26.6 | 64.1 | 53.2 | 5.4 | 15.8 | 2.1 | 0.9 | 10.1 | 1.6 | 0.0 | 0.2 | 0.0 | 0.2 | 556.9 |
| oak | 6.9 | 7.1 | 28.2 | 315.1 | 19.5 | 99.1 | 61.4 | 3.5 | 14.4 | 0.5 | 0.2 | 3.2 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 559.4 |
| maple | 9.7 | 5.8 | 28.3 | 243.3 | 16.4 | 57.4 | 46.7 | 2.6 | 7.0 | 4.3 | 1.8 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 423.5 |
| pine | 2.5 | 7.6 | 17.2 | 78.8 | 4.0 | 40.1 | 27.7 | 8.8 | 9.5 | 15.0 | 6.4 | 6.8 | 10.7 | 1.4 | 7.1 | 1.8 | 4.0 | 249.3 |

**TABLE B-1:** Soil samples of the Blautopf Catchment, concentrations in µg kg$^{-1}$.

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ΣPAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BP SH 1 0-25 | 2.5 | 4.3 | 5.1 | 24.2 | 1.8 | 30.7 | 22.5 | 10.3 | 20.3 | 33.8 | 14.5 | 21.0 | 13.9 | 2.4 | 24.6 | 6.3 | 26.4 | 264.6 |
| BP SH 1 26-50 | 1.1 | 3.2 | 3.1 | 8.3 | 0.4 | 3.8 | 2.9 | 1.7 | 3.2 | 5.7 | 2.4 | 3.7 | 2.8 | 0.6 | 6.1 | 1.6 | 6.1 | 56.9 |
| BP SH 1 > 50 | 0.4 | 0.8 | 1.1 | 0.8 | 0.3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.4 | 0.1 | 0.4 | 5.6 |
| BP BS 1 0-10 | 1.3 | 5.6 | 11.2 | 19.7 | 1.6 | 25.1 | 16.5 | 8.1 | 18.3 | 24.0 | 10.3 | 12.0 | 8.5 | 1.6 | 16.3 | 3.0 | 13.1 | 196.4 |
| BP BS 1 10-25 | 1.1 | 2.8 | 4.7 | 13.7 | 1.2 | 17.4 | 11.5 | 6.3 | 12.9 | 16.2 | 7.0 | 9.0 | 5.0 | 0.9 | 8.7 | 1.5 | 7.1 | 126.9 |
| BP BS 1 > 40 | 0.6 | 2.9 | 5.6 | 5.8 | 0.5 | 6.1 | 3.8 | 2.3 | 5.9 | 8.8 | 3.8 | 5.3 | 2.0 | 0.4 | 4.4 | 0.7 | 3.9 | 63.0 |
| BPVK 1 0-20 | 1.5 | 1.7 | 5.9 | 29.8 | 2.4 | 48.3 | 35.2 | 20.6 | 32.9 | 44.9 | 19.2 | 23.8 | 20.9 | 4.7 | 21.9 | 4.7 | 19.6 | 338.0 |
| BPVK 1 40-50 | 0.1 | 0.2 | 0.4 | 6.2 | 0.2 | 1.4 | 0.9 | 0.4 | 1.1 | 3.9 | 1.7 | 0.9 | 0.4 | 0.1 | 0.8 | 0.2 | 0.8 | 19.8 |
| BPVK 1 70 | 0.2 | 0.4 | 0.8 | 8.7 | 0.2 | 1.7 | 1.0 | 0.5 | 1.0 | 4.6 | 2.0 | 0.9 | 0.5 | 0.2 | 1.1 | 0.3 | 0.8 | 25.0 |
| BPVK 1 80 cm | 0.5 | 1.5 | 2.6 | 6.8 | 0.2 | 1.7 | 1.2 | 0.5 | 1.6 | 2.5 | 1.1 | 1.4 | 0.4 | 0.1 | 1.4 | 0.2 | 1.0 | 24.8 |
| BPVK 2 10-20 | 0.8 | 0.6 | 2.0 | 12.7 | 0.5 | 10.6 | 7.1 | 3.3 | 8.5 | 10.8 | 4.6 | 6.3 | 3.5 | 0.6 | 6.2 | 1.0 | 7.0 | 86.2 |
| BPVK 2 50-60 | 0.5 | 1.6 | 2.0 | 4.0 | 0.3 | 3.5 | 2.4 | 1.0 | 3.5 | 4.5 | 1.9 | 2.6 | 1.1 | 0.0 | 2.7 | 0.4 | 2.6 | 34.6 |
| BP VK 2 > 60 | 17.5 | 88.9 | 80.5 | 49.1 | 5.5 | 35.3 | 22.5 | 15.3 | 40.1 | 48.5 | 20.8 | 26.3 | 7.6 | 1.4 | 29.1 | 5.2 | 29.7 | 523.1 |
| BPVK 3 0-10 | 9.9 | 1.9 | 7.3 | 89.1 | 8.6 | 171.5 | 120.9 | 53.5 | 110.7 | 181.4 | 77.7 | 84.5 | 62.8 | 7.9 | 80.5 | 14.8 | 57.3 | 1140.4 |
| BPVK 3 10-15 | 0.3 | 0.4 | 0.4 | 8.3 | 0.4 | 11.7 | 8.4 | 6.0 | 9.3 | 16.0 | 6.9 | 8.3 | 6.4 | 0.5 | 6.4 | 1.0 | 6.0 | 96.6 |
| BPVK 3 20-25 | 0.3 | 2.5 | 3.8 | 6.4 | 0.3 | 2.4 | 1.6 | 0.6 | 1.7 | 2.3 | 1.0 | 1.3 | 0.8 | 0.0 | 1.6 | 0.0 | 1.5 | 27.9 |
| BPVK 3 30-35 | 0.3 | 0.0 | 2.9 | 4.6 | 0.2 | 0.5 | 0.3 | 0.1 | 0.3 | 1.8 | 0.8 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 12.1 |
| BP LTH Sp 2 5-10 | 3.9 | 1.8 | 2.8 | 39.3 | 6.0 | 121.6 | 95.5 | 13.2 | 62.7 | 94.6 | 40.5 | 55.8 | 60.7 | 15.5 | 42.3 | 10.2 | 39.1 | 705.4 |
| BP LTH Sp 2 10-20 | 0.8 | 40.4 | 80.1 | 576.4 | 90.1 | 422.3 | 364.8 | 173.4 | 163.9 | 263.3 | 112.8 | 173.7 | 217.4 | 43.5 | 115.8 | 54.2 | 114.4 | 3007.6 |

**TABLE B-1:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ΣPAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BP LTH Sp 1 0-5 | 4.1 | 5.3 | 7.0 | 48.5 | 7.9 | 137.0 | 106.0 | 60.9 | 73.1 | 80.3 | 34.4 | 49.0 | 49.5 | 16.5 | 34.1 | 8.3 | 32.9 | 754.8 |
| BP LTH Sp 1 10-18 | 0.8 | 4.5 | 7.6 | 7.3 | 1.3 | 14.6 | 11.2 | 6.9 | 8.2 | 14.6 | 6.2 | 8.6 | 9.0 | 2.1 | 8.7 | 2.1 | 8.1 | 121.7 |
| BP GH Sei 0-4 | 2.6 | 3.0 | 7.5 | 32.2 | 4.6 | 57.7 | 40.4 | 19.4 | 27.4 | 48.1 | 20.6 | 31.1 | 22.6 | 3.9 | 18.7 | 3.9 | 20.1 | 363.7 |
| BP GH Sei 5-10 | 2.0 | 4.2 | 7.9 | 28.3 | 3.3 | 51.2 | 35.1 | 15.7 | 26.6 | 44.1 | 18.9 | 28.3 | 21.7 | 3.6 | 19.3 | 4.4 | 21.3 | 336.1 |
| BP GH Tie 0-22 | 2.0 | 1.3 | 2.3 | 36.5 | 3.5 | 57.0 | 41.1 | 20.2 | 27.7 | 47.4 | 20.3 | 30.4 | 24.9 | 4.5 | 18.8 | 4.4 | 16.6 | 358.8 |
| BP GH Tie >22 | 0.8 | 2.3 | 4.3 | 11.9 | 2.0 | 28.8 | 23.3 | 10.9 | 12.8 | 17.7 | 7.6 | 10.5 | 11.1 | 2.2 | 7.4 | 1.9 | 6.1 | 161.6 |
| EGBO 1 | 4.1 | 1.2 | 4.7 | 66.3 | 5.9 | 114.4 | 84.8 | 59.0 | 75.9 | 111.6 | 47.8 | 71.1 | 67.5 | 23.3 | 55.9 | 14.9 | 42.6 | 850.7 |
| EGBO 2 | 7.0 | 2.1 | 11.2 | 154.5 | 14.7 | 171.1 | 117.5 | 105.8 | 114.4 | 164.3 | 70.4 | 92.9 | 97.5 | 38.0 | 63.6 | 13.2 | 50.0 | 1288.3 |
| EGBO 3 | 17.8 | 4.6 | 13.0 | 202.3 | 16.7 | 399.7 | 281.9 | 232.8 | 263.7 | 376.7 | 161.5 | 208.6 | 231.1 | 105.9 | 186.0 | 57.9 | 132.4 | 2892.5 |
| EGBO 4 | 33.5 | 5.5 | 25.0 | 310.1 | 31.1 | 451.4 | 326.6 | 316.8 | 297.6 | 446.3 | 191.3 | 261.6 | 306.4 | 114.3 | 219.9 | 61.6 | 160.4 | 3559.3 |
| EGBO 5 | 1.7 | 0.8 | 3.0 | 24.2 | 3.4 | 41.7 | 31.3 | 28.1 | 31.4 | 47.5 | 20.4 | 24.6 | 26.4 | 17.4 | 21.3 | 6.2 | 14.2 | 343.6 |
| EGBO 6 | 9.8 | 2.6 | 7.0 | 110.6 | 20.6 | 233.3 | 194.6 | 174.4 | 158.8 | 229.6 | 98.4 | 150.7 | 160.5 | 59.6 | 140.0 | 37.1 | 113.4 | 1901.0 |
| EGBO 7 | 1.7 | 0.6 | 4.5 | 19.0 | 2.1 | 32.3 | 23.5 | 12.8 | 17.2 | 22.5 | 9.6 | 13.8 | 11.7 | 4.6 | 11.6 | 2.8 | 9.1 | 199.5 |
| EGBO 8 | 10.8 | 5.8 | 17.2 | 167.1 | 22.7 | 324.2 | 241.3 | 196.8 | 213.2 | 294.0 | 126.0 | 171.0 | 180.2 | 68.1 | 102.4 | 28.6 | 74.2 | 2243.5 |
| EGBO 9 | 47.6 | 10.5 | 31.6 | 579.0 | 48.1 | 1042.8 | 739.6 | 484.6 | 512.5 | 692.5 | 296.8 | 394.4 | 447.7 | 162.9 | 352.4 | 94.0 | 248.7 | 6185.5 |
| EGBO 10 | 123.5 | 77.0 | 203.7 | 3241.1 | 501.9 | 3865.7 | 2443.3 | 2681.8 | 2531.7 | 1423.0 | 609.8 | 648.3 | 759.4 | 336.0 | 265.4 | 65.6 | 186.1 | 19963 |
| EGBO 11 | 3.8 | 1.3 | 5.5 | 51.8 | 5.4 | 73.8 | 52.4 | 44.6 | 52.8 | 76.7 | 32.9 | 45.4 | 45.0 | 16.6 | 34.6 | 8.9 | 25.9 | 577.4 |
| EGBO 12 | 1.2 | 0.0 | 3.2 | 25.3 | 3.2 | 32.8 | 21.2 | 12.3 | 25.5 | 16.8 | 7.2 | 9.7 | 2.4 | 0.9 | 10.0 | 3.6 | 7.0 | 182.3 |
| EGBO 13 | 5.0 | 1.6 | 4.4 | 33.2 | 3.7 | 58.5 | 42.3 | 36.6 | 41.8 | 66.3 | 28.4 | 38.9 | 40.9 | 14.7 | 32.9 | 7.6 | 25.1 | 482.0 |
| EGBO 14 | 18.3 | 17.7 | 31.4 | 688.4 | 103.2 | 1338.2 | 889.6 | 728.0 | 783.8 | 1042.5 | 446.8 | 516.4 | 569.0 | 233.0 | 238.3 | 55.3 | 188.2 | 7888.3 |
| EGBO 15 | 2.3 | 0.9 | 5.6 | 17.1 | 1.7 | 21.1 | 14.0 | 16.6 | 22.4 | 25.2 | 10.8 | 15.0 | 13.6 | 6.8 | 7.8 | 2.7 | 6.1 | 189.8 |

**TABLE B-2:** Concentrations of the loam samples (ng L$^{-1}$).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ΣPAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LP LTHa | 1 | 1 | n.d. | 10 | 1 | 14 | 11 | 7 | 7 | 15 | 6 | 9 | 6 | 2 | 12 | 5 | 1n.d. | 117 |
| LP LTHb | n.d. | 1 | 2 | 11 | 1 | 9 | 7 | 5 | 5 | 8 | 3 | 5 | 4 | 1 | 6 | 3 | 5 | 76 |
| LP SHa | n.d. | 1 | n.d. | 3 | n.d. | 3 | 3 | 1 | 1 | 2 | 1 | 2 | 1 | n.d. | 3 | 1 | 2 | 24 |
| LP SHb | n.d. | n.d. | n.d. | 1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2 |

**TABLE B-3:** Leaching test (ASE) of the soil samples, concentrations in ng L$^{-1}$.

| sample | temp [°C] | duration [min] | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | Σ PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LTH-Sp 2 M1 | 20 | 30 | 0 | 0 | 0 | 21 | 0 | 24 | 0 | 0 | 0 | 16 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 68 |
| LTH-Sp 2 M2 | 20 | 99 | 0 | 0 | 0 | 0 | 0 | 30 | 0 | 0 | 0 | 16 | 7 | 0 | 0 | 0 | 0 | 0 | 0 | 53 |
| LTH-Sp 2 M3 | 40 | 99 | 0 | 0 | 0 | 35 | 0 | 45 | 25 | 0 | 0 | 28 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 145 |
| LTH-Sp 2 M4 | 47 | 99 | 0 | 0 | 0 | 53 | 0 | 67 | 41 | 0 | 0 | 32 | 14 | 0 | 0 | 0 | 0 | 0 | 0 | 207 |
| LTH-Sp 2 M5 | 53 | 30 | 0 | 0 | 0 | 49 | 0 | 66 | 36 | 0 | 0 | 38 | 16 | 0 | 0 | 0 | 0 | 0 | 0 | 206 |
| LTH-Sp 2 M6 | 53 | 99 | 0 | 0 | 0 | 50 | 0 | 68 | 42 | 47 | 39 | 55 | 24 | 0 | 0 | 0 | 0 | 0 | 0 | 325 |
| LTH-Sp 2 M7 | 64 | 99 | 0 | 0 | 0 | 65 | 0 | 68 | 45 | 54 | 44 | 52 | 22 | 0 | 0 | 0 | 0 | 0 | 0 | 351 |
| LTH-Sp 2 M8 | 75 | 99 | 0 | 0 | 0 | 81 | 0 | 101 | 58 | 44 | 0 | 86 | 37 | 0 | 0 | 0 | 0 | 0 | 0 | 408 |
| LTH-Sp 2 M9 | 87 | 99 | 0 | 0 | 0 | 117 | 0 | 162 | 84 | 112 | 80 | 118 | 50 | 0 | 0 | 0 | 43 | 66 | 74 | 907 |
| LTH-Sp 2 M10 | 100 | 99 | 0 | 0 | 0 | 142 | 0 | 163 | 107 | 109 | 77 | 122 | 52 | 0 | 0 | 0 | 40 | 69 | 83 | 963 |
| | | | | | | | | | | | | | | | | | | | | |
| Sei 0-4 M1 | 20 | 30 | 10 | 10 | 23 | 98 | 2 | 11 | 7 | 3 | 2 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 169 |
| Sei 0-4 M2 | 20 | 99 | 4 | 2 | 8 | 35 | 1 | 8 | 5 | 3 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 70 |
| Sei 0-4 M3 | 40 | 99 | 4 | 5 | 8 | 35 | 1 | 8 | 6 | 3 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 73 |
| Sei 0-4 M4 | 47 | 99 | 4 | 0 | 7 | 32 | 1 | 6 | 5 | 4 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 62 |
| Sei 0-4 M5 | 53 | 30 | 4 | 0 | 7 | 35 | 0 | 8 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 63 |
| Sei 0-4 M6 | 53 | 99 | 3 | 0 | 6 | 27 | 0 | 7 | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 49 |

**TABLE B-3:** Continuation

| sample | temp [°C] | duration [min] | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | Σ PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sei 0-4 M7 | 64 | 99 | 4 | 0 | 8 | 43 | 2 | 16 | 10 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 86 |
| Sei 0-4 M8 | 75 | 99 | 7 | 8 | 13 | 69 | 3 | 25 | 16 | 7 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 149 |
| Sei 0-4 M9 | 87 | 99 | 8 | 16 | 23 | 136 | 7 | 57 | 34 | 9 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 296 |
| Sei 0-4 M10 | 100 | 99 | 14 | 30 | 34 | 246 | 10 | 160 | 92 | 13 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 609 |
| Tie 0-22 M1 | 20 | 30 | 17 | 0 | 0 | 22 | 3 | 11 | 0 | 0 | 0 | 6 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 153 |
| Tie 0-22 M2 | 20 | 99 | 20 | 0 | 0 | 26 | 0 | 18 | 0 | 0 | 0 | 10 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 194 |
| Tie 0-22 M3 | 40 | 99 | 41 | 0 | 0 | 36 | 0 | 24 | 0 | 0 | 0 | 17 | 7 | 0 | 0 | 0 | 0 | 0 | 19 | 258 |
| Tie 0-22 M4 | 47 | 99 | 57 | 0 | 0 | 28 | 8 | 0 | 0 | 0 | 0 | 21 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 167 |
| Tie 0-22 M5 | 53 | 30 | 61 | 0 | 0 | 32 | 6 | 33 | 0 | 33 | 28 | 44 | 19 | 0 | 0 | 0 | 0 | 0 | 29 | 447 |
| Tie 0-22 M6 | 53 | 99 | 70 | 0 | 0 | 38 | 0 | 54 | 0 | 37 | 37 | 49 | 21 | 0 | 0 | 0 | 37 | 37 | 50 | 718 |
| Tie 0-22 M7 | 64 | 99 | 0 | 0 | 0 | 44 | 0 | 106 | 0 | 47 | 39 | 59 | 25 | 0 | 36 | 0 | 22 | 39 | 44 | 767 |
| Tie 0-22 M8 | 75 | 99 | 50 | 0 | 0 | 36 | 0 | 44 | 0 | 35 | 29 | 43 | 18 | 0 | 17 | 0 | 0 | 40 | 29 | 486 |
| Tie 0-22 M9 | 87 | 99 | 56 | 0 | 0 | 55 | 11 | 44 | 30 | 77 | 59 | 74 | 32 | 0 | 37 | 0 | 0 | 63 | 55 | 592 |
| Tie 0-22 M10 | 100 | 99 | 44 | 0 | 0 | 84 | 18 | 55 | 25 | 76 | 59 | 75 | 32 | 0 | 36 | 0 | 35 | 55 | 57 | 759 |
| EGBO 10 M1 | 20 | 30 | 22 | 8 | 0 | 35 | 22 | 24 | 14 | 6 | 0 | 4 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 140 |
| EGBO 10 M2 | 20 | 99 | 11 | 9 | 6 | 31 | 12 | 18 | 10 | 5 | 0 | 3 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 109 |
| EGBO 10 M3 | 40 | 99 | 23 | 27 | 26 | 119 | 27 | 72 | 43 | 10 | 7 | 8 | 3 | 5 | 0 | 13 | 0 | 0 | 0 | 384 |
| EGBO 10 M4 | 47 | 99 | 45 | 73 | 56 | 273 | 37 | 133 | 77 | 18 | 15 | 12 | 5 | 8 | 11 | 10 | 0 | 0 | 0 | 774 |
| EGBO 10 M5 | 53 | 30 | 50 | 99 | 86 | 400 | 54 | 178 | 101 | 14 | 11 | 7 | 3 | 4 | 0 | 0 | 0 | 0 | 0 | 1006 |
| EGBO 10 M6 | 53 | 99 | 52 | 85 | 93 | 469 | 55 | 193 | 111 | 16 | 8 | 5 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 1093 |
| EGBO 10 M7 | 64 | 99 | 66 | 147 | 171 | 769 | 85 | 316 | 179 | 21 | 12 | 5 | 2 | 3 | 0 | 0 | 0 | 0 | 0 | 1775 |
| EGBO 10 M8 | 75 | 99 | 78 | 155 | 167 | 892 | 99 | 379 | 225 | 25 | 19 | 7 | 3 | 4 | 0 | 0 | 0 | 0 | 0 | 2053 |

**TABLE B-3:** Continuation

| sample | temp [°C] | duration [min] | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | Σ PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EGBO 10 M9 | 87 | 99 | 93 | 209 | 252 | 1300 | 139 | 597 | 348 | 42 | 38 | 7 | 3 | 4 | 5 | 7 | 0 | 0 | 0 | 3043 |
| EGBO 10 M10 | 100 | 99 | 164 | 311 | 403 | 2359 | 254 | 1199 | 712 | 80 | 75 | 14 | 6 | 8 | 9 | 9 | 0 | 0 | 0 | 5602 |

**Table C-1:** Results from the passive sampler [ng $L^{-1}$] in the Laichinger Tiefenhöhle (LTH).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30.04.-06.06-04 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 8 |
| LTH I | 0 | 1 | 1 | 11 | 2 | 28 | 19 | 11 | 21 | 5 | 2 | 11 | 10 | 3 | 13 | 3 | 8 | 149 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 2 | 1 | 1 | 1 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 12 |
| 06.06.-27.08.04 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| LTH I | 0 | 0 | 0 | 2 | 0 | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 16 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 3 | 2 | 2 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 19 |
| 27.08.04-30.01.05 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| LTH I | 1 | 0 | 0 | 7 | 1 | 13 | 10 | 8 | 7 | 11 | 5 | 5 | 8 | 2 | 8 | 4 | 6 | 93 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 8 |
| 30.01.-24.03.05 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 0 | 1 | 1 | 9 | 2 | 29 | 22 | 16 | 12 | 15 | 7 | 8 | 12 | 4 | 11 | 4 | 8 | 159 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 |
| 24.03.-19.07.05 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 0 | 2 | 1 | 13 | 3 | 39 | 30 | 30 | 19 | 30 | 13 | 17 | 23 | 5 | 19 | 6 | 13 | 263 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |

**Table C-1:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 19.07.-24.09.05 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 0 | 0 | 0 | 4 | 1 | 10 | 8 | 7 | 5 | 7 | 3 | 4 | 5 | 1 | 4 | 1 | 3 | 64 |
| LTH II | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| 24.09.-11.11.05 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 11 |
| 11.11.05-15.01.06 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 0 | 0 | 0 | 1 | 0 | 4 | 3 | 2 | 1 | 2 | 1 | 1 | 2 | 0 | 1 | 0 | 1 | 21 |
| LTH II | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| LTH gas | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| 15.01.-10.03.06 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| LTH I | 0 | 1 | 1 | 5 | 1 | 13 | 10 | 7 | 6 | 7 | 3 | 4 | 5 | 2 | 4 | 1 | 4 | 74 |
| LTH II | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| LTH gas | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 10.03.-30.04.06 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 1 | 2 | 1 | 20 | 4 | 61 | 45 | 35 | 29 | 41 | 18 | 25 | 31 | 8 | 24 | 7 | 20 | 371 |

**Table C-1:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LTH II | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| LTH gas | 0 | 1 | 0 | 4 | 1 | 10 | 7 | 6 | 5 | 5 | 2 | 3 | 4 | 1 | 2 | 1 | 2 | 54 |
| 30.04.-19.07.06 | | | | | | | | | | | | | | | | | | |
| LTH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| LTH I | 0 | 1 | 0 | 4 | 1 | 11 | 8 | 7 | 5 | 8 | 3 | 5 | 6 | 1 | 4 | 1 | 3 | 69 |
| LTH II | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| LTH gas | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |

**Table C-2:** Results from the passive sampler [ng $L^{-1}$] in the Hawaii-Schacht (HWS).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30.04.-13.06.04 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| HWS I | 0 | 0 | 0 | 2 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 7 |
| HWS II | 1 | 4 | 3 | 7 | 1 | 3 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 30 |
| 13.06.04-28.01.05 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| HWS I | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| HWS II | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 28.01.-18.02.05 | | | | | | | | | | | | | | | | | | |
| HWS blank | 1 | 0 | 2 | 8 | 1 | 2 | 1 | 1 | 2 | 2 | 1 | 1 | 1 | 0 | 2 | 0 | 1 | 27 |
| HWS I | 20 | 20 | 39 | 163 | 26 | 112 | 90 | 48 | 51 | 60 | 26 | 41 | 41 | 15 | 41 | 12 | 41 | 846 |

**Table C-2:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HWS II | 1 | 0 | 2 | 9 | 1 | 8 | 6 | 4 | 4 | 5 | 2 | 3 | 3 | 1 | 4 | 1 | 4 | 57 |
| 20.02.- 19.04.05 | | | | | | | | | | | | | | | | | | |
| HWS I | 0 | 0 | 0 | 2 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | 10 |
| 05.03.-19.04.05 | | | | | | | | | | | | | | | | | | |
| HWS II | 1 | 0 | 7 | 9 | 1 | 5 | 4 | 2 | 2 | 3 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 43 |
| 19.04.-19.07.05 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| HWS I | 0 | 0 | 0 | 1 | 0 | 2 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 11 |
| HWS II | 0 | 0 | 0 | 2 | 0 | 4 | 3 | 2 | 2 | 4 | 2 | 2 | 2 | 1 | 2 | 0 | 3 | 29 |
| 19.07.-25.09.05 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| HWS I | 0 | 0 | 0 | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 11 |
| HWS II | 1 | 0 | 1 | 31 | 1 | 3 | 3 | 2 | 1 | 2 | 1 | 2 | 2 | 0 | 2 | 0 | 2 | 54 |
| 25.09.05-14.01.06 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| HWS I | 0 | 0 | 0 | 2 | 0 | 3 | 3 | 1 | 1 | 2 | 1 | 2 | 2 | 0 | 1 | 0 | 1 | 22 |
| HWS II | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 14.01.-10.03.06 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |

**Table C-2:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HWS I | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| HWS II | 2 | 2 | 2 | 7 | 3 | 10 | 9 | 2 | 4 | 4 | 2 | 3 | 2 | 1 | 2 | 1 | 3 | 59 |
| 10.03.-30.04.06 | | | | | | | | | | | | | | | | | | |
| HWS blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| HWS I | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 8 |
| HWS II | 1 | 1 | 1 | 2 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 11 |

**Table C-3:** Results from the passive sampler [ng $L^{-1}$] in the Sontheimer Höhle (SH).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 19.03.-02.04.04 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| SH III | 0 | 1 | 1 | 3 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| 02.04.-30.04.04 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| SH I | 0 | 0 | 0 | 3 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| SH III | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| 30.04.-05.06.04 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| SH I | 0 | 0 | 1 | 4 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 |
| SH III | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 6 |

**Table C-3:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 05.06.-27.08.04 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 0 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| SH I | 0 | 0 | 1 | 3 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 |
| SH III | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| 27.08.04-29.01.05 | | | | | | | | | | | | | | | | | | |
| SH blank | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| SH I | 0 | 0 | 0 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 7 |
| SH III | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 5 |
| 29.01.-18.03.05 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| SH I | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 9 |
| SH III | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 5 |
| 18.03.-19.07.05 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| SH III | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 3 |
| SH I | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| 19.07.05-30.03.06 | | | | | | | | | | | | | | | | | | |
| SH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| SH I | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 9 |
| SH III | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |

**Table C-4:** Results from the passive sampler [ng L$^{-1}$] in the Steingau-Höhle (StH).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 09.07.04-28.01.05 | | | | | | | | | | | | | | | | | | |
| StH blank | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| StH I | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 9 |
| StH II | 2 | 0 | 0 | 7 | 1 | 3 | 3 | 2 | 5 | 5 | 2 | 2 | 3 | 1 | 4 | 4 | 3 | 46 |
| 28.01.-19.07.05 | | | | | | | | | | | | | | | | | | |
| StH blank | 0 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| StH I | 0 | 0 | 0 | 2 | 0 | 4 | 3 | 2 | 2 | 3 | 1 | 1 | 2 | 0 | 2 | 0 | 2 | 25 |
| StH II | 0 | 0 | 0 | 2 | 0 | 5 | 4 | 3 | 3 | 5 | 2 | 2 | 3 | 1 | 4 | 1 | 3 | 37 |
| 19.07.05-30.04.06 | | | | | | | | | | | | | | | | | | |
| StH blank | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| StH I | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| StH II | 0 | 0 | 0 | 2 | 0 | 3 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 19 |

**Table C-5:** Results from the water samples [ng L$^{-1}$] in the Laichinger Tiefenhöhle (LTH).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13.03.-21.03.05 | 4 | 13 | 9 | 179 | 37 | 697 | 535 | 351 | 334 | 468 | 200 | 255 | 370 | 83 | 262 | 98 | 205 | 4099 |
| 21.03.-24.03.05 | 19 | 64 | 47 | 807 | 178 | 2980 | 2277 | 1475 | 1383 | 1962 | 841 | 1060 | 1618 | 336 | 1146 | 437 | 878 | 17508 |
| 24.03.-28.03.05 | 4 | 11 | 8 | 138 | 30 | 543 | 420 | 267 | 257 | 357 | 153 | 193 | 284 | 64 | 198 | 75 | 155 | 3157 |
| 05.04.-09.04.05 | 0 | 0 | 0 | 6 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 |
| 09.04.-19.04.05 | 1 | 2 | 2 | 31 | 6 | 124 | 97 | 59 | 60 | 81 | 35 | 44 | 60 | 15 | 42 | 16 | 34 | 707 |
| 19.04.-25.04.05 | 0 | 1 | 1 | 8 | 2 | 24 | 18 | 11 | 9 | 14 | 6 | 8 | 11 | 2 | 7 | 3 | 5 | 130 |

**Table C-5:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25.04.-25.05.05 | 0 | 0 | 0 | 2 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| 18.06.-25.06.05 | 0 | 2 | 1 | 10 | 2 | 36 | 28 | 17 | 17 | 22 | 9 | 12 | 15 | 4 | 10 | 4 | 9 | 198 |
| 25.06.-08.07.05 | 0 | 0 | 0 | 4 | 1 | 11 | 8 | 4 | 4 | 6 | 2 | 3 | 4 | 1 | 3 | 1 | 3 | 56 |
| 08.07.-19.07.05 | 0 | 0 | 0 | 4 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| 19.07.-25.07.05 | 1 | 0 | 0 | 3 | 1 | 12 | 10 | 10 | 12 | 50 | 22 | 35 | 47 | 15 | 55 | 18 | 43 | 332 |
| 25.07.-14.08.05 | 0 | 0 | 0 | 4 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 14.08.-24.08.05 | 0 | 0 | 1 | 11 | 2 | 33 | 25 | 16 | 15 | 18 | 8 | 10 | 13 | 3 | 8 | 3 | 8 | 175 |
| 24.08.-25.08.05 | 0 | 0 | 1 | 6 | 2 | 16 | 12 | 7 | 7 | 8 | 4 | 5 | 6 | 2 | 4 | 2 | 3 | 83 |
| 25.08.-06.09.05 | 2 | 4 | 9 | 32 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 47 |
| 06.09.-14.09.05 | 0 | 0 | 0 | 2 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| 14.09.-24.09.05 | 0 | 0 | 0 | 4 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7 |
| 24.09.-29.09.05 | 1 | 3 | 2 | 37 | 7 | 103 | 78 | 44 | 39 | 54 | 23 | 28 | 39 | 9 | 25 | 10 | 18 | 521 |
| 08.10.-15.10.05 | 0 | 0 | 0 | 4 | 0 | 2 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| 15.10.-21.10.05 | 0 | 0 | 0 | 3 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| 21.10.-28.10.05 | 0 | 0 | 0 | 4 | 1 | 12 | 9 | 6 | 6 | 7 | 3 | 4 | 5 | 1 | 3 | 1 | 3 | 66 |
| 28.10.-11.11.05 | 1 | 2 | 2 | 30 | 7 | 89 | 67 | 39 | 38 | 49 | 21 | 27 | 32 | 9 | 23 | 8 | 18 | 461 |
| 11.11.-19.11.05 | 4 | 16 | 10 | 205 | 49 | 615 | 475 | 369 | 319 | 488 | 209 | 314 | 386 | 99 | 364 | 101 | 302 | 4326 |
| 19.11.-27.11.05 | 1 | 6 | 5 | 82 | 20 | 263 | 197 | 123 | 124 | 153 | 66 | 91 | 111 | 32 | 86 | 30 | 75 | 1466 |
| 27.11.-01.12.05 | 4 | 3 | 3 | 35 | 10 | 125 | 95 | 60 | 60 | 87 | 37 | 52 | 65 | 17 | 49 | 16 | 43 | 760 |
| 01.12.-11.12.05 | 1 | 4 | 3 | 54 | 13 | 154 | 117 | 85 | 70 | 94 | 40 | 54 | 69 | 15 | 44 | 15 | 35 | 868 |
| 11.12.-18.12.05 | 1 | 5 | 5 | 78 | 18 | 243 | 181 | 108 | 109 | 134 | 57 | 80 | 95 | 27 | 73 | 28 | 62 | 1304 |
| 18.12.-29.12.05 | 1 | 8 | 7 | 127 | 30 | 396 | 296 | 183 | 182 | 222 | 95 | 132 | 159 | 43 | 113 | 44 | 95 | 2132 |
| 29.12.05-08.01.06 | 1 | 5 | 5 | 87 | 18 | 260 | 192 | 119 | 118 | 155 | 66 | 86 | 118 | 27 | 85 | 32 | 70 | 1444 |
| 08.01.-15.01.06 | 1 | 3 | 3 | 48 | 11 | 151 | 114 | 68 | 68 | 90 | 39 | 51 | 66 | 16 | 49 | 19 | 43 | 839 |

**Table C-5:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 15.01.-22.01.06 | 1 | 6 | 6 | 98 | 20 | 296 | 219 | 130 | 127 | 167 | 72 | 92 | 126 | 30 | 90 | 18 | 73 | 1571 |
| 22.01.-31.01.06 | 1 | 3 | 4 | 60 | 12 | 181 | 136 | 82 | 81 | 103 | 44 | 57 | 77 | 18 | 52 | 20 | 43 | 973 |
| 31.01.-11.02.06 | 1 | 4 | 4 | 56 | 12 | 173 | 129 | 78 | 77 | 99 | 42 | 55 | 73 | 18 | 51 | 21 | 42 | 935 |
| 11.02.-16.02.06 | 2 | 13 | 13 | 230 | 48 | 743 | 555 | 333 | 321 | 449 | 192 | 251 | 355 | 75 | 251 | 43 | 199 | 4075 |
| 16.02.-19.02.06 | 1 | 3 | 2 | 42 | 9 | 130 | 96 | 56 | 54 | 71 | 30 | 39 | 55 | 12 | 38 | 15 | 30 | 682 |
| 19.02.-26.02.06 | 1 | 4 | 3 | 54 | 12 | 169 | 127 | 76 | 73 | 95 | 41 | 52 | 72 | 16 | 49 | 19 | 40 | 901 |
| 26.02.-02.03.06 | 1 | 4 | 3 | 55 | 13 | 176 | 133 | 83 | 81 | 107 | 46 | 60 | 80 | 19 | 56 | 22 | 44 | 982 |
| 02.03.-10.03.06 | 1 | 5 | 5 | 86 | 19 | 284 | 216 | 121 | 109 | 148 | 64 | 77 | 110 | 25 | 78 | 30 | 57 | 1434 |
| 10.03.-16.03.06 | 2 | 12 | 12 | 215 | 47 | 652 | 475 | 282 | 272 | 320 | 137 | 186 | 228 | 63 | 159 | 63 | 129 | 3253 |
| 16.03.-23.03.06 | 1 | 11 | 10 | 162 | 36 | 491 | 367 | 222 | 219 | 260 | 111 | 153 | 187 | 52 | 134 | 51 | 110 | 2577 |
| 23.03.-28.03.06 | 24 | 200 | 179 | 2571 | 548 | 6895 | 4940 | 3161 | 2902 | 3397 | 1456 | 1934 | 2484 | 622 | 1587 | 522 | 1281 | 34703 |
| 28.03.-29.03.06 | 4 | 17 | 17 | 242 | 56 | 699 | 527 | 336 | 298 | 381 | 163 | 194 | 292 | 69 | 209 | 78 | 149 | 3732 |
| 29.03.-30.03.06 | 0 | 2 | 2 | 21 | 4 | 64 | 48 | 30 | 25 | 32 | 14 | 19 | 23 | 7 | 17 | 5 | 13 | 327 |
| 30.03.-04.04.06 | 0 | 2 | 2 | 25 | 6 | 81 | 62 | 39 | 35 | 47 | 20 | 24 | 36 | 9 | 25 | 9 | 19 | 440 |
| 04.04.-12.04.06 | 0 | 1 | 0 | 9 | 2 | 20 | 15 | 9 | 9 | 11 | 5 | 6 | 7 | 2 | 5 | 2 | 4 | 105 |
| 12.04.-19.04.06 | 3 | 13 | 13 | 194 | 42 | 571 | 424 | 276 | 245 | 325 | 139 | 169 | 252 | 52 | 167 | 61 | 121 | 3068 |
| 19.04.-26.04.06 | 1 | 12 | 8 | 95 | 22 | 263 | 198 | 126 | 114 | 144 | 62 | 74 | 106 | 24 | 69 | 26 | 51 | 1392 |
| 26.04.-30.04.06 | 0 | 1 | 1 | 13 | 3 | 37 | 27 | 16 | 15 | 18 | 8 | 9 | 13 | 3 | 8 | 3 | 6 | 181 |
| 06.05.-09.05.06 | 1 | 6 | 5 | 82 | 19 | 248 | 187 | 117 | 106 | 135 | 58 | 70 | 99 | 23 | 62 | 24 | 46 | 1288 |
| 09.05.-14.05.06 | 0 | 1 | 1 | 22 | 5 | 62 | 47 | 30 | 27 | 36 | 15 | 19 | 25 | 6 | 17 | 4 | 13 | 331 |
| 14.05.-20.05.06 | 0 | 1 | 1 | 9 | 2 | 27 | 20 | 14 | 12 | 16 | 7 | 9 | 11 | 3 | 7 | 3 | 6 | 147 |
| 20.05.-28.05.06 | 0 | 1 | 1 | 15 | 4 | 45 | 35 | 23 | 19 | 25 | 11 | 14 | 18 | 4 | 11 | 4 | 9 | 241 |
| 28.05.-12.06.06 | 2 | 8 | 8 | 133 | 30 | 371 | 280 | 200 | 149 | 201 | 86 | 115 | 150 | 32 | 91 | 29 | 71 | 1957 |
| 12.06.-16.06.06 | 0 | 1 | 1 | 8 | 2 | 22 | 17 | 12 | 10 | 13 | 6 | 7 | 10 | 2 | 6 | 2 | 5 | 125 |

**Table C-5:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16.06.-30.06.06 | 0 | 1 | 1 | 18 | 4 | 54 | 42 | 28 | 23 | 30 | 13 | 17 | 22 | 5 | 13 | 4 | 11 | 286 |
| 30.06.-07.07.06 | 0 | 1 | 1 | 7 | 2 | 22 | 17 | 12 | 10 | 14 | 6 | 7 | 10 | 2 | 6 | 2 | 5 | 125 |
| 07.07.-19.07.06 | 0 | 0 | 0 | 7 | 2 | 19 | 15 | 8 | 7 | 9 | 4 | 5 | 6 | 2 | 4 | 2 | 4 | 94 |

**Table C-6:** Results from the water samplers [ng $L^{-1}$] in the Hawaii-Schacht (HWS).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14.03.-19.03.05 | 2 | 1 | 0 | 2 | 3 | 9 | 7 | 4 | 5 | 8 | 3 | 6 | 5 | 1 | 5 | 2 | 6 | 69 |
| 24.03.-28.03.05 | 1 | 0 | 0 | 2 | 3 | 5 | 4 | 3 | 3 | 4 | 2 | 3 | 3 | 1 | 3 | 0 | 4 | 39 |
| 04.04.-10.04.05 | 0 | 0 | 0 | 4 | 2 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| 19.04.-25.04.05 | 0 | 0 | 0 | 3 | 3 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| 08.07.-19.07.05 | 13 | 5 | 3 | 26 | 20 | 74 | 65 | 40 | 58 | 127 | 54 | 101 | 131 | 33 | 101 | 30 | 88 | 970 |
| 19.07.-14.08.05 | 1 | 0 | 0 | 2 | 3 | 4 | 3 | 2 | 2 | 2 | 1 | 2 | 2 | 0 | 1 | 0 | 2 | 28 |
| 14.08.-24.08.05 | 4 | 0 | 0 | 12 | 7 | 32 | 26 | 14 | 17 | 22 | 9 | 15 | 14 | 3 | 12 | 4 | 14 | 206 |
| 24.08.-06.09.05 | 1 | 0 | 0 | 2 | 3 | 6 | 5 | 3 | 4 | 4 | 2 | 3 | 3 | 1 | 3 | 1 | 3 | 45 |
| 06.09.-14.09.05 | 2 | 0 | 0 | 5 | 4 | 13 | 10 | 6 | 7 | 8 | 4 | 6 | 6 | 1 | 5 | 2 | 6 | 84 |
| 14.09.-19.09.05 | 1 | 0 | 0 | 1 | 3 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 |
| 25.09.-01.10.05 | 0 | 0 | 0 | 1 | 2 | 2 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 11 |
| 02.10.-08.10.05 | 0 | 0 | 0 | 1 | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 14 |
| 08.10.-15.10.05 | 0 | 0 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 10 |
| 15.10.-21.10.05 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| 21.10.-28.10.05 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 28.10.-11.11.05 | 1 | 0 | 0 | 1 | 3 | 3 | 2 | 2 | 1 | 2 | 1 | 1 | 1 | 0 | 2 | 0 | 2 | 22 |
| 11.11.-24.11.05 | 1 | 2 | 0 | 1 | 3 | 2 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 15 |

**Table C-6:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24.11.-10.12.05 | 1 | 2 | 0 | 1 | 3 | 4 | 3 | 2 | 2 | 3 | 1 | 2 | 2 | 1 | 2 | 0 | 2 | 29 |
| 10.12.-30.12.05 | 1 | 1 | 0 | 1 | 3 | 4 | 3 | 2 | 2 | 3 | 1 | 2 | 2 | 1 | 1 | 0 | 2 | 29 |
| 30.12.05-14.01.06 | 1 | 1 | 0 | 5 | 4 | 2 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 25 |
| 14.01.-20.01.06 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4 |
| 20.01.-06.02.06 | 0 | 1 | 0 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 8 |
| 06.02.-17.02.06 | 1 | 1 | 0 | 4 | 2 | 5 | 4 | 2 | 2 | 3 | 1 | 2 | 2 | 0 | 2 | 1 | 2 | 34 |
| 17.02.-24.02.06 | 1 | 0 | 0 | 1 | 2 | 2 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 16 |
| 24.02.-03.03.06 | 1 | 1 | 0 | 0 | 2 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 11 |
| 03.03.-10.03.06 | 1 | 1 | 0 | 3 | 4 | 11 | 9 | 6 | 6 | 9 | 4 | 6 | 6 | 2 | 5 | 2 | 5 | 80 |
| 10.03.-17.03.06 | 1 | 1 | 0 | 2 | 2 | 5 | 4 | 2 | 2 | 3 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 32 |
| 17.03.-23.03.06 | 1 | 0 | 0 | 2 | 3 | 6 | 5 | 3 | 3 | 4 | 2 | 3 | 2 | 1 | 2 | 1 | 2 | 37 |
| 23.03.-28.03.06 | 2 | 3 | 2 | 59 | 12 | 88 | 66 | 44 | 42 | 40 | 17 | 26 | 28 | 8 | 26 | 8 | 25 | 496 |
| 28.03.-29.03.06 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 29.03.-07.04.06 | 0 | 0 | 0 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 14 |
| 07.04.-13.04.06 | 1 | 0 | 0 | 3 | 2 | 8 | 6 | 3 | 4 | 5 | 2 | 3 | 3 | 1 | 3 | 1 | 3 | 46 |
| 13.04.-19.04.06 | 0 | 0 | 2 | 2 | 1 | 6 | 5 | 3 | 3 | 3 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 38 |
| 19.04.-26.04.06 | 0 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 15 |
| 26.04.-30.04.06 | 1 | 0 | 0 | 3 | 2 | 8 | 6 | 3 | 4 | 6 | 2 | 4 | 3 | 1 | 3 | 1 | 3 | 52 |

**Table C-7:** Results from the water samples [ng $L^{-1}$] in the Sontheimer Höhle (SH).

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14.03.-04.04.05 | 0 | 0 | 0 | 7 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 |
| 04.04.-09.04.05 | 0 | 0 | 0 | 5 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |

**Table C-7:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 09.04.-19.04.05 | 1 | 0 | 0 | 1 | 0 | 3 | 3 | 3 | 3 | 3 | 1 | 2 | 2 | 1 | 2 | 0 | 2 | 26 |
| 06.05.-17.05.05 | 1 | 2 | 1 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| 19.07.-27.07.05 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 6 |
| 15.08.-24.08.05 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| 24.08.-06.09.05 | 0 | 0 | 1 | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 11 |
| 06.09.-14.09.05 | 1 | 1 | 1 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| 14.09.-03.10.05 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| 21.10.-30.10.05 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 19.11.-12.12.05 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 10 |
| 01.12.-16.01.06 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 3 | 0 | 0 | 10 |
| 16.01.-17.02.06 | 0 | 0 | 1 | 3 | 0 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 15 |
| 17.02.-13.03.06 | 1 | 1 | 1 | 3 | 1 | 6 | 6 | 3 | 3 | 5 | 2 | 4 | 4 | 1 | 4 | 1 | 4 | 51 |
| 13.03.-18.03.06 | 0 | 0 | 0 | 4 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 18.03.-23.03.06 | 0 | 0 | 0 | 2 | 0 | 4 | 4 | 2 | 2 | 3 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 29 |
| 23.03.-29.03.06 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 |
| 29.03.-30.03.06 | 0 | 0 | 2 | 1 | 0 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 9 |

**Table D-1:** Concentrations of PAHs in the groundwater [ng $L^{-1}$] of Blautopf Spring, measured with the time integrated sampler BT K1-g.

| | **Any** | **Ace** | **Fln** | **Phe** | **Ant** | **Fth** | **Py** | **BaA** | **Chr** | **BbF** | **BkF** | **BeP** | **BaP** | **Per** | **Indo** | **DahA** | **BghiP** | **∑PAHs** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 05.03.-29.03.05 | 0.1 | 0.0 | 0.1 | 0.7 | 0.1 | 1.4 | 1.0 | 0.6 | 0.6 | 0.7 | 0.3 | 0.4 | 0.5 | 0.2 | 0.7 | 0.2 | 0.6 | 8.4 |
| 30.03.-19.04.05 | 0.0 | 0.0 | 0.0 | 0.3 | 0.1 | 0.4 | 0.3 | 0.2 | 0.2 | 0.3 | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 | 0.0 | 0.1 | 2.6 |
| 19.04.-06.05.05 | 0.0 | 0.0 | 0.0 | 0.7 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 2.0 |
| 06.05.-16.05.05 | 0.1 | 0.0 | 0.1 | 0.6 | 0.1 | 0.8 | 0.7 | 0.4 | 0.4 | 0.6 | 0.3 | 0.4 | 0.4 | 0.2 | 0.5 | 0.1 | 0.4 | 5.8 |
| 16.05.-02.07.05 | 0.0 | 0.0 | 0.0 | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 1.7 |
| 02.07.-22.07.05 | 0.0 | 0.0 | 0.1 | 0.3 | 0.1 | 0.3 | 0.3 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 | 0.3 | 0.1 | 0.3 | 3.1 |
| 08.08.-24.08.05 | 0.0 | 0.0 | 0.0 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 1.6 |
| 24.08.-15.09.05 | 0.0 | 0.0 | 0.1 | 0.4 | 0.2 | 0.6 | 0.5 | 0.3 | 0.3 | 0.5 | 0.2 | 0.3 | 0.3 | 0.1 | 0.5 | 0.1 | 0.4 | 5.0 |
| 25.09.-15.10.05 | 0.0 | 0.0 | 0.0 | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 1.5 |
| 15.10.-29.10.05 | 0.1 | 0.0 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.3 |
| 29.10.-12.11.05 | 0.0 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 |
| 02.12.-24.12.05 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| 17.02.-06.03.06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 1.0 |
| 10.03.-29.03.06 | 1.0 | 0.2 | 0.4 | 4.2 | 0.8 | 8.4 | 6.3 | 3.7 | 4.3 | 6.0 | 2.6 | 3.7 | 4.1 | 1.0 | 4.2 | 1.3 | 4.1 | 56.2 |
| 29.03.-28.04.06 | 0.2 | 0.1 | 0.1 | 1.7 | 0.2 | 1.8 | 1.5 | 0.8 | 1.0 | 1.3 | 0.6 | 0.8 | 0.9 | 0.2 | 1.0 | 0.3 | 1.0 | 13.4 |
| 28.04.-13.05.06 | 0.0 | 0.0 | 0.0 | 0.3 | 0.1 | 0.5 | 0.4 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.2 | 0.0 | 0.2 | 2.7 |
| 13.05.-28.05.06 | 0.1 | 0.1 | 0.1 | 0.8 | 0.2 | 0.3 | 0.3 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.0 | 0.1 | 0.0 | 0.1 | 3.0 |
| 28.05.-19.06.06 | 0.0 | 0.0 | 0.0 | 0.6 | 0.2 | 0.3 | 0.3 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 2.5 |
| 19.06.-07.07.06 | 0.0 | 0.0 | 0.0 | 0.7 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 2.2 |
| 07.07.-20.07.06 | 0.1 | 0.0 | 0.0 | 0.5 | 0.2 | 0.5 | 0.4 | 0.2 | 0.3 | 0.4 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.1 | 0.2 | 3.7 |

**Table D-2:** Concentrations of PAHs in the groundwater [ng $L^{-1}$] of Blautopf Spring, measured with the time integrated sampler BT K2-g.

| | **Any** | **Ace** | **Fln** | **Phe** | **Ant** | **Fth** | **Py** | **BaA** | **Chr** | **BbF** | **BkF** | **BeP** | **BaP** | **Per** | **Indo** | **DahA** | **BghiP** | **∑PAHs** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 05.03.-19.04.05 | 0.1 | 0.0 | 0.1 | 0.6 | 0.1 | 1.0 | 0.8 | 0.5 | 0.5 | 0.8 | 0.4 | 0.5 | 0.6 | 0.3 | 0.6 | 0.1 | 0.5 | 7.5 |
| 19.40.-06.05.05 | 0.0 | 0.0 | 0.0 | 0.6 | 0.1 | 0.5 | 0.5 | 0.3 | 0.4 | 0.5 | 0.2 | 0.3 | 0.4 | 0.2 | 0.4 | 0.1 | 0.3 | 5.0 |
| 16.05.-02.07.05 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 1.3 |
| 02.07.-22.07.05 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 1.2 |
| 22.07.-29.08.05 | 0.0 | 0.0 | 0.1 | 0.6 | 0.2 | 0.6 | 0.5 | 0.3 | 0.4 | 0.6 | 0.2 | 0.4 | 0.4 | 0.1 | 0.5 | 0.1 | 0.5 | 5.6 |
| 29.08.-15.09.05 | 0.0 | 0.0 | 0.0 | 0.2 | 0.2 | 0.4 | 0.8 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 | 0.2 | 0.0 | 0.3 | 3.4 |
| 15.09.-15.10.05 | 0.0 | 0.0 | 0.2 | 0.3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.3 | 0.1 | 0.0 | 0.2 | 0.0 | 0.2 | 0.1 | 0.2 | 0.2 | 2.4 |
| 15.10.-24.11.05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 02.12.-24.12.05 | 0.1 | 0.1 | 0.1 | 0.3 | 0.4 | 0.3 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 2.4 |
| 17.02.-06.03.06 | 0.4 | 0.1 | 0.1 | 2.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 4.0 |
| 10.03.-29.03.06 | 0.7 | 0.2 | 0.3 | 5.7 | 0.6 | 7.1 | 5.3 | 3.0 | 3.6 | 4.9 | 2.1 | 3.0 | 3.3 | 0.8 | 3.4 | 1.0 | 3.2 | 48.3 |
| 29.03.-28.04.06 | 0.1 | 0.0 | 0.1 | 1.2 | 0.2 | 1.5 | 1.2 | 0.6 | 0.8 | 1.1 | 0.5 | 0.7 | 0.7 | 0.2 | 0.9 | 0.3 | 0.8 | 10.8 |
| 28.04.-13.05.06 | 0.0 | 0.0 | 0.0 | 0.3 | 0.1 | 0.3 | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 2.2 |
| 13.05.-28.05.06 | 0.0 | 0.0 | 0.0 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| 28.05.-19.06.06 | 0.0 | 0.0 | 0.0 | 1.5 | 0.2 | 0.3 | 0.3 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 3.6 |
| 19.06.-07.07.06 | 0.0 | 0.0 | 0.0 | 0.9 | 0.1 | 0.3 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 2.8 |
| 07.07.-20.07.06 | 0.0 | 0.0 | 0.0 | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 1.6 |

**Table D-3:** Concentrations of PAHs in the groundwater [ng $L^{-1}$] of Blautopf Spring, measured with the time integrated sampler BT K3-g.

| | **Any** | **Ace** | **Fln** | **Phe** | **Ant** | **Fth** | **Py** | **BaA** | **Chr** | **BbF** | **BkF** | **BeP** | **BaP** | **Per** | **Indo** | **DahA** | **BghiP** | **∑PAHs** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 05.03.-02.07.05 | 0.0 | 0.0 | 0.1 | 0.3 | 0.1 | 0.6 | 0.5 | 0.3 | 0.3 | 0.5 | 0.2 | 0.3 | 0.3 | 0.1 | 0.3 | 0.1 | 0.3 | 4.5 |
| 02.07.-15.09.05 | 0.0 | 0.0 | 0.0 | 0.2 | 0.1 | 0.3 | 0.2 | 0.1 | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 | 0.0 | 0.2 | 2.3 |
| 24.11.05-29.03.06 | 0.1 | 0.0 | 0.1 | 0.5 | 0.2 | 0.9 | 0.7 | 0.4 | 0.5 | 0.8 | 0.3 | 0.5 | 0.5 | 0.1 | 0.6 | 0.2 | 0.6 | 7.0 |

**Table D-4:** Concentrations of PAHs in the water samples [ng L$^{-1}$].

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 20.02.05 | 0.6 | 0.0 | 0.7 | 2.4 | 2.0 | 1.5 | 1.7 | 0.5 | 0.5 | 0.9 | 0.4 | 0.7 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 12.4 |
| 03.03.05 | 0.3 | 0.0 | 0.5 | 54.5 | 2.9 | 0.6 | 0.8 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 60.0 |
| 06.03.05 | 0.4 | 0.0 | 0.4 | 9.3 | 2.3 | 0.6 | 0.7 | 0.4 | 0.4 | 0.5 | 0.2 | 0.4 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 15.8 |
| 23.03.05 | 0.0 | 0.0 | 0.0 | 0.5 | 1.0 | 1.6 | 1.2 | 0.8 | 0.9 | 1.2 | 0.5 | 0.9 | 0.9 | 0.2 | 0.8 | 0.0 | 1.2 | 11.7 |
| 24.03.05 | 0.8 | 0.0 | 0.0 | 0.9 | 1.8 | 2.3 | 2.2 | 1.7 | 1.2 | 2.3 | 1.0 | 1.6 | 1.5 | 0.4 | 0.0 | 0.0 | 0.0 | 17.9 |
| 27.03.05 | 0.5 | 0.0 | 0.0 | 1.1 | 1.9 | 1.8 | 1.8 | 1.4 | 0.8 | 1.6 | 0.7 | 1.4 | 1.2 | 0.0 | 1.0 | 0.0 | 1.0 | 16.2 |
| 28.03.05 | 0.7 | 0.2 | 0.0 | 1.0 | 1.5 | 2.1 | 1.8 | 1.2 | 1.0 | 1.6 | 0.7 | 1.2 | 1.2 | 0.3 | 1.0 | 0.0 | 1.1 | 16.6 |
| 29.03.05 | 0.0 | 0.0 | 0.0 | 0.5 | 1.4 | 0.3 | 0.7 | 0.5 | 0.0 | 0.1 | 0.1 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.0 |
| 07.04.05 | 0.4 | 0.0 | 0.2 | 0.5 | 1.3 | 0.8 | 0.8 | 0.7 | 0.0 | 0.6 | 0.3 | 0.6 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 6.8 |
| 23.04.05 | 0.0 | 0.0 | 0.0 | 0.4 | 0.2 | 0.2 | 0.3 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.5 |
| 18.06.05 | 0.4 | 0.0 | 0.2 | 0.5 | 1.6 | 0.2 | 0.5 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.8 |
| 01.07.05 | 0.0 | 0.0 | 0.0 | 0.4 | 0.7 | 0.3 | 0.3 | 0.5 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 | 0.4 | 0.0 | 3.6 |
| 02.07.05 | 0.6 | 0.0 | 0.0 | 0.5 | 1.9 | 0.3 | 0.4 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.0 |
| 27.07.05 | 0.0 | 0.0 | 0.0 | 0.4 | 1.4 | 0.4 | 0.4 | 0.3 | 0.2 | 0.3 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.4 |
| 15.08.05 | 0.5 | 0.0 | 0.0 | 0.7 | 2.4 | 0.4 | 0.7 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.2 |
| 24.08.05 | 1.1 | 0.0 | 0.0 | 2.3 | 3.5 | 5.9 | 5.2 | 2.7 | 2.2 | 4.4 | 1.9 | 3.0 | 3.0 | 0.8 | 2.4 | 0.8 | 2.5 | 41.4 |
| 25.08.05 | 0.4 | 0.4 | 0.3 | 1.6 | 1.0 | 2.8 | 2.1 | 2.1 | 1.7 | 2.6 | 1.1 | 1.0 | 1.7 | 0.3 | 1.5 | 1.2 | 1.8 | 23.5 |
| 26.08.05 | 0.7 | 0.0 | 0.3 | 0.7 | 2.7 | 1.6 | 1.5 | 1.2 | 0.0 | 1.3 | 0.5 | 1.1 | 0.9 | 0.0 | 0.9 | 0.0 | 1.0 | 14.2 |
| 29.08.05 | 0.6 | 0.0 | 0.3 | 0.6 | 2.5 | 0.6 | 0.7 | 0.8 | 0.2 | 0.4 | 0.2 | 0.6 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 7.8 |
| 13.09.05 | 0.2 | 0.2 | 0.2 | 0.5 | 0.4 | 1.1 | 0.9 | 0.9 | 0.7 | 1.0 | 0.4 | 0.3 | 0.6 | 0.1 | 0.6 | 0.5 | 0.7 | 9.2 |
| 15.09.05 | 0.0 | 0.0 | 0.0 | 0.4 | 0.7 | 0.4 | 0.4 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.1 |
| 25.09.05 | 0.0 | 0.0 | 0.0 | 2.1 | 0.8 | 0.9 | 0.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.4 |
| 25.09.05 | 0.0 | 0.0 | 0.0 | 0.4 | 1.0 | 0.4 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.5 |

**Table D-4:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30.09.05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 30.09.05 | 0.0 | 0.0 | 0.0 | 2.3 | 0.9 | 0.9 | 0.5 | 0.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5.3 |
| 05.10.05 | 0.0 | 0.0 | 0.0 | 3.9 | 0.9 | 1.5 | 1.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.3 |
| 15.10.05 | 0.0 | 0.0 | 0.0 | 0.5 | 0.7 | 0.4 | 0.3 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.2 |
| 15.10.05 | 0.0 | 0.0 | 0.3 | 1.4 | 0.5 | 0.5 | 0.4 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.4 |
| 22.10.05 | 0.0 | 0.0 | 0.0 | 0.6 | 0.2 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.1 |
| 22.10.05 | 0.0 | 0.0 | 0.0 | 0.9 | 0.7 | 0.6 | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.1 |
| 29.10.05 | 0.0 | 0.0 | 0.0 | 0.2 | 0.4 | 0.3 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.1 |
| 29.10.05 | 0.2 | 0.7 | 0.9 | 3.1 | 1.0 | 1.7 | 1.8 | 0.9 | 0.5 | 0.5 | 0.2 | 0.0 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 12.0 |
| 12.11.05 | 0.1 | 0.0 | 0.1 | 0.4 | 0.5 | 0.5 | 0.5 | 0.3 | 0.3 | 0.5 | 0.2 | 0.3 | 0.2 | 0.1 | 0.3 | 0.2 | 0.2 | 4.6 |
| 12.11.05 | 0.0 | 0.0 | 0.0 | 23.5 | 19.8 | 1.3 | 1.4 | 1.1 | 0.7 | 1.3 | 0.6 | 0.8 | 0.9 | 0.3 | 0.0 | 0.0 | 0.0 | 51.6 |
| 19.11.05 | 0.2 | 0.0 | 0.1 | 0.4 | 0.7 | 0.3 | 0.3 | 0.3 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.6 |
| 24.11.05 | 0.0 | 0.0 | 0.0 | 0.7 | 0.8 | 0.6 | 0.4 | 0.0 | 0.0 | 0.8 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.7 |
| 24.11.05 | 0.0 | 0.0 | 0.0 | 0.3 | 0.7 | 0.5 | 0.5 | 0.8 | 0.4 | 0.6 | 0.2 | 0.4 | 0.4 | 0.1 | 0.4 | 0.1 | 0.4 | 5.7 |
| 01.12.05 | 0.0 | 0.0 | 0.0 | 1.1 | 0.3 | 0.1 | 0.2 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.9 |
| 16.02.06 | 0.2 | 0.0 | 0.1 | 0.5 | 1.0 | 0.5 | 0.5 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.3 | 0.0 | 0.2 | 4.1 |
| 17.02.06 | 0.2 | 0.0 | 0.2 | 0.8 | 0.9 | 0.9 | 1.7 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 | 0.3 | 0.0 | 0.2 | 6.5 |
| 18.02.06 | 0.1 | 0.0 | 0.1 | 0.4 | 0.4 | 0.4 | 0.3 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 | 0.1 | 0.0 | 0.3 | 0.0 | 0.2 | 3.0 |
| 19.02.06 | 0.3 | 0.0 | 0.3 | 0.8 | 0.8 | 0.7 | 0.5 | 0.3 | 0.4 | 0.5 | 0.2 | 0.4 | 0.3 | 0.1 | 0.0 | 0.2 | 1.1 | 6.8 |
| 24.02.06 | 0.1 | 0.0 | 0.0 | 0.6 | 1.1 | 0.5 | 0.6 | 0.3 | 0.3 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 4.2 |
| 09.03.2006 21:00 | 0.1 | 0.0 | 0.0 | 1.1 | 1.0 | 0.6 | 0.7 | 0.4 | 0.2 | 0.4 | 0.2 | 0.3 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 5.2 |
| 10.03.2006 08:30 | 0.7 | 0.0 | 0.3 | 1.8 | 1.3 | 5.4 | 4.4 | 2.1 | 2.6 | 3.6 | 1.5 | 2.0 | 2.4 | 0.6 | 2.0 | 0.5 | 1.7 | 33.1 |
| 10.03.2006 15:30 | 1.1 | 0.0 | 0.4 | 3.5 | 1.6 | 10.1 | 7.9 | 4.2 | 5.1 | 6.8 | 2.9 | 4.0 | 4.7 | 1.1 | 4.1 | 1.1 | 3.4 | 61.9 |

**Table D-4:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11.03.2006 09:00 | 1.1 | 0.0 | 0.4 | 2.9 | 1.9 | 7.5 | 6.5 | 3.4 | 4.8 | 5.2 | 2.2 | 3.1 | 3.8 | 0.9 | 2.9 | 1.1 | 2.9 | 50.5 |
| 11.03.2006 17:15 | 0.7 | 0.0 | 0.0 | 2.1 | 1.4 | 4.6 | 4.1 | 2.2 | 2.7 | 3.6 | 1.5 | 2.1 | 2.2 | 0.6 | 2.2 | 0.0 | 1.9 | 31.9 |
| 12.03.2006 18:00 | 0.3 | 0.0 | 0.2 | 0.9 | 1.1 | 1.8 | 1.8 | 0.9 | 0.9 | 1.3 | 0.5 | 0.7 | 0.8 | 0.2 | 0.8 | 0.0 | 0.7 | 13.2 |
| 13.03.2006 10:00 | 0.2 | 0.0 | 0.2 | 0.9 | 1.1 | 1.8 | 1.7 | 0.8 | 0.8 | 1.0 | 0.4 | 0.6 | 0.7 | 0.2 | 0.7 | 0.0 | 0.6 | 11.7 |
| 15.03.06 | 0.2 | 0.0 | 0.2 | 0.6 | 0.8 | 0.9 | 0.7 | 0.4 | 0.3 | 0.4 | 0.2 | 0.3 | 0.2 | 0.1 | 0.3 | 0.0 | 0.3 | 5.7 |
| 17.03.06 | 0.6 | 0.2 | 0.3 | 0.9 | 0.6 | 0.6 | 0.5 | 0.3 | 0.3 | 0.2 | 0.1 | 0.2 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 5.1 |
| 23.03.06 | 0.2 | 0.0 | 0.1 | 0.7 | 0.7 | 0.6 | 0.4 | 0.4 | 0.3 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 | 0.2 | 0.0 | 0.2 | 4.6 |
| 24.03.06 | 0.2 | 0.0 | 0.1 | 0.4 | 0.6 | 0.7 | 0.5 | 0.3 | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 | 0.2 | 0.0 | 0.2 | 4.3 |
| 25.03.06 | 0.3 | 0.0 | 0.2 | 0.4 | 0.7 | 0.7 | 0.5 | 0.6 | 0.4 | 0.6 | 0.2 | 0.4 | 0.4 | 0.1 | 0.4 | 0.0 | 0.4 | 6.3 |
| 26.03.2006 09:30 | 1.0 | 0.0 | 0.2 | 4.0 | 1.6 | 11.8 | 9.0 | 4.5 | 5.8 | 7.3 | 3.1 | 4.7 | 5.1 | 1.3 | 4.2 | 1.0 | 4.0 | 68.7 |
| 26.03.2006 17:40 | 2.0 | 0.3 | 0.6 | 9.2 | 2.6 | 24.7 | 18.6 | 9.2 | 12.0 | 15.4 | 6.6 | 9.3 | 10.4 | 2.5 | 8.9 | 2.4 | 8.1 | 143.0 |
| 27.03.2006 08:35 | 3.3 | 0.4 | 1.0 | 13.0 | 3.4 | 39.2 | 30.3 | 15.3 | 19.1 | 25.6 | 11.0 | 15.5 | 17.8 | 4.5 | 15.1 | 4.0 | 13.4 | 232.0 |
| 27.03.2006 13:00 | 5.2 | 0.3 | 1.0 | 15.0 | 5.1 | 48.4 | 37.0 | 19.0 | 23.9 | 33.1 | 14.2 | 19.1 | 23.0 | 5.4 | 20.0 | 6.1 | 18.1 | 293.9 |
| 27.03.2006 18:30 | 3.4 | 0.4 | 1.1 | 13.3 | 4.0 | 39.4 | 30.1 | 15.7 | 19.7 | 27.3 | 11.7 | 15.5 | 18.6 | 4.1 | 15.5 | 4.9 | 13.8 | 238.6 |
| 27.03.2006 22:15 | 2.1 | 0.3 | 0.6 | 7.5 | 2.6 | 22.5 | 17.3 | 9.1 | 12.3 | 16.3 | 7.0 | 10.3 | 11.3 | 2.6 | 10.4 | 2.9 | 9.2 | 144.1 |
| 28.03.2006 09:15 | 2.9 | 0.3 | 0.8 | 10.7 | 3.5 | 31.3 | 24.3 | 12.7 | 16.2 | 21.3 | 9.1 | 12.2 | 14.3 | 3.8 | 11.4 | 3.6 | 10.7 | 189.0 |
| 28.03.2006 14:30 | 2.2 | 0.4 | 0.7 | 9.0 | 2.7 | 25.4 | 19.7 | 10.4 | 13.5 | 17.6 | 7.5 | 10.8 | 12.2 | 3.0 | 10.5 | 3.0 | 9.5 | 157.9 |
| 28.03.2006 19:30 | 2.0 | 0.3 | 0.5 | 7.4 | 2.3 | 22.6 | 17.8 | 9.1 | 11.8 | 15.4 | 6.6 | 9.5 | 10.9 | 2.7 | 9.5 | 3.1 | 8.9 | 140.3 |
| 28.03.2006 23:00 | 2.1 | 0.4 | 1.0 | 11.5 | 3.3 | 37.3 | 28.4 | 15.0 | 17.8 | 21.4 | 9.2 | 12.6 | 14.7 | 3.8 | 11.8 | 3.2 | 10.2 | 203.6 |
| 29.03.2006 09:00 | 1.3 | 0.2 | 0.5 | 7.3 | 1.9 | 15.0 | 11.7 | 6.0 | 7.8 | 10.3 | 4.4 | 6.4 | 7.1 | 1.7 | 6.2 | 1.7 | 5.7 | 95.1 |
| 29.03.2006 14:40 | 1.5 | 0.0 | 0.4 | 4.5 | 1.9 | 12.9 | 10.5 | 5.1 | 6.8 | 8.7 | 3.7 | 5.0 | 5.7 | 1.6 | 4.6 | 1.4 | 4.3 | 78.6 |
| 29.03.2006 20:30 | 0.1 | 0.0 | 0.1 | 0.4 | 0.1 | 1.1 | 0.9 | 0.4 | 0.5 | 0.5 | 0.2 | 0.2 | 0.6 | 0.5 | 0.1 | 0.4 | 0.1 | 6.1 |
| 30.03.2006 16:30 | 0.7 | 0.0 | 0.3 | 2.5 | 0.8 | 6.1 | 4.8 | 2.3 | 3.1 | 3.9 | 1.7 | 2.6 | 2.7 | 0.7 | 2.3 | 0.7 | 2.2 | 37.3 |

**Table D-4:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 31.03.06 | 0.5 | 0.2 | 0.2 | 2.2 | 1.1 | 6.2 | 4.8 | 2.9 | 3.3 | 4.4 | 1.9 | 2.2 | 3.0 | 0.6 | 2.3 | 1.2 | 2.4 | 39.3 |
| 01.04.06 | 0.5 | 0.1 | 0.2 | 2.0 | 1.0 | 4.8 | 3.9 | 2.2 | 2.5 | 3.6 | 1.5 | 1.8 | 2.5 | 0.4 | 2.0 | 1.1 | 2.0 | 32.1 |
| 02.04.06 | 0.5 | 0.0 | 0.0 | 3.6 | 1.2 | 4.3 | 3.5 | 1.9 | 2.3 | 2.8 | 1.2 | 1.6 | 1.7 | 0.5 | 1.6 | 0.0 | 1.4 | 28.1 |
| 03.04.06 | 0.4 | 0.0 | 0.2 | 1.2 | 0.8 | 2.9 | 2.3 | 1.5 | 1.6 | 2.5 | 1.1 | 1.1 | 1.6 | 0.3 | 1.3 | 0.8 | 1.5 | 21.1 |
| 04.04.06 | 0.3 | 0.0 | 0.0 | 25.6 | 1.7 | 2.3 | 1.9 | 1.2 | 1.4 | 1.9 | 0.8 | 0.8 | 1.1 | 0.2 | 0.9 | 0.6 | 1.2 | 41.9 |
| 05.04.06 | 0.4 | 0.0 | 0.2 | 1.3 | 0.9 | 2.2 | 1.8 | 1.2 | 1.3 | 1.8 | 0.8 | 0.8 | 1.1 | 0.2 | 0.9 | 0.8 | 1.2 | 16.9 |
| 06.04.06 | 0.3 | 0.0 | 0.0 | 0.9 | 0.8 | 2.1 | 1.6 | 0.9 | 1.1 | 1.3 | 0.6 | 0.8 | 0.9 | 0.2 | 0.8 | 0.0 | 0.7 | 13.0 |
| 07.04.06 | 0.4 | 0.0 | 0.0 | 0.9 | 0.8 | 1.6 | 1.3 | 0.7 | 0.8 | 1.0 | 0.4 | 0.6 | 0.6 | 0.2 | 0.5 | 0.0 | 0.6 | 10.3 |
| 08.04.06 | 0.3 | 0.0 | 0.0 | 0.7 | 0.8 | 1.9 | 1.4 | 0.9 | 0.9 | 1.2 | 0.5 | 0.8 | 0.8 | 0.3 | 0.8 | 0.0 | 0.7 | 12.1 |
| 09.04.06 | 0.3 | 0.0 | 0.1 | 0.7 | 0.8 | 1.6 | 1.3 | 0.9 | 0.9 | 1.4 | 0.6 | 0.6 | 0.9 | 0.2 | 0.9 | 0.7 | 1.0 | 12.9 |
| 10.04.06 | 0.2 | 0.0 | 0.1 | 0.7 | 0.7 | 1.6 | 1.2 | 0.9 | 0.9 | 1.4 | 0.6 | 0.6 | 0.9 | 0.1 | 0.9 | 0.8 | 1.0 | 12.8 |
| 11.04.06 | 0.0 | 0.0 | 0.0 | 0.7 | 0.8 | 1.6 | 1.2 | 0.9 | 0.9 | 1.2 | 0.5 | 0.5 | 0.8 | 0.1 | 0.7 | 0.5 | 0.8 | 11.4 |
| 12.04.06 | 0.2 | 0.0 | 0.2 | 0.9 | 0.9 | 1.5 | 1.2 | 1.0 | 0.9 | 1.3 | 0.5 | 0.7 | 0.8 | 0.2 | 0.7 | 0.5 | 0.8 | 12.3 |
| 13.04.06 | 0.2 | 0.0 | 0.0 | 1.1 | 1.0 | 1.1 | 0.9 | 0.6 | 0.6 | 0.7 | 0.3 | 0.5 | 0.4 | 0.1 | 0.0 | 0.0 | 0.4 | 7.9 |
| 14.04.06 | 0.2 | 0.0 | 0.0 | 3.3 | 0.8 | 1.8 | 1.5 | 1.1 | 1.1 | 1.5 | 0.7 | 0.7 | 0.9 | 0.2 | 0.9 | 0.6 | 1.1 | 16.5 |
| 15.04.06 | 0.0 | 0.0 | 61.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 61.0 |
| 16.04.06 | 0.3 | 0.1 | 0.1 | 0.9 | 0.9 | 2.2 | 1.8 | 1.2 | 1.3 | 1.9 | 0.8 | 0.8 | 1.2 | 0.2 | 1.0 | 0.7 | 1.2 | 16.7 |
| 17.04.06 | 0.2 | 0.1 | 0.2 | 0.9 | 0.4 | 2.0 | 1.6 | 1.3 | 1.2 | 1.8 | 0.8 | 0.7 | 1.1 | 0.2 | 1.0 | 0.8 | 1.0 | 15.3 |
| 18.04.06 | 0.3 | 0.2 | 0.3 | 1.1 | 0.5 | 1.3 | 1.2 | 0.9 | 0.8 | 1.2 | 0.5 | 0.4 | 0.7 | 0.0 | 0.6 | 0.6 | 0.8 | 11.6 |
| 19.04.06 | 0.2 | 0.0 | 0.2 | 1.8 | 0.8 | 2.4 | 1.6 | 1.1 | 1.3 | 1.5 | 0.6 | 0.6 | 0.9 | 0.2 | 0.7 | 0.7 | 0.9 | 15.7 |
| 20.04.06 | 0.2 | 0.1 | 0.1 | 0.7 | 0.6 | 1.3 | 1.0 | 0.8 | 0.7 | 1.1 | 0.5 | 0.4 | 0.7 | 0.1 | 0.6 | 0.6 | 0.8 | 10.4 |
| 21.04.06 | 0.2 | 0.0 | 0.0 | 0.5 | 0.7 | 0.7 | 0.6 | 0.5 | 0.3 | 0.4 | 0.2 | 0.2 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 4.5 |
| 22.04.06 | 0.2 | 0.1 | 0.1 | 0.8 | 0.7 | 1.2 | 0.9 | 0.8 | 0.7 | 1.0 | 0.4 | 0.4 | 0.7 | 0.1 | 0.6 | 0.6 | 0.7 | 10.0 |

**Table D-4:** Continuation

| | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP | ∑PAHs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 23.04.06 | 0.2 | 0.0 | 0.0 | 0.9 | 0.7 | 1.2 | 0.9 | 0.6 | 0.5 | 0.6 | 0.3 | 0.4 | 0.4 | 0.1 | 0.0 | 0.0 | 0.3 | 7.1 |
| 24.04.06 | 0.3 | 0.0 | 0.0 | 0.8 | 0.6 | 1.4 | 0.9 | 0.5 | 0.6 | 0.7 | 0.3 | 0.4 | 0.4 | 0.1 | 0.0 | 0.0 | 0.4 | 7.4 |
| 25.04.06 | 0.2 | 0.0 | 0.0 | 0.8 | 0.8 | 1.0 | 0.8 | 0.5 | 0.4 | 0.6 | 0.3 | 0.4 | 0.4 | 0.1 | 0.0 | 0.0 | 0.4 | 6.8 |
| 26.04.06 | 0.2 | 0.0 | 0.1 | 0.8 | 0.7 | 1.3 | 0.9 | 0.7 | 0.5 | 0.7 | 0.3 | 0.4 | 0.5 | 0.1 | 0.4 | 0.0 | 0.4 | 8.0 |
| 27.04.06 | 0.0 | 0.0 | 0.0 | 0.7 | 0.8 | 1.2 | 1.0 | 0.8 | 0.7 | 1.1 | 0.5 | 0.4 | 0.6 | 0.1 | 0.6 | 0.7 | 0.7 | 9.7 |
| 28.04.06 | 0.4 | 0.0 | 0.2 | 2.3 | 0.8 | 2.6 | 2.0 | 1.2 | 1.4 | 2.1 | 0.9 | 1.0 | 1.4 | 0.2 | 1.2 | 0.7 | 1.4 | 20.0 |
| 29.04.06 | 0.2 | 0.1 | 0.1 | 0.7 | 0.9 | 1.2 | 1.1 | 0.8 | 0.7 | 1.0 | 0.4 | 0.3 | 0.6 | 0.0 | 0.6 | 0.5 | 0.7 | 9.7 |
| 05.05.06 | 0.0 | 0.0 | 0.0 | 1.0 | 0.8 | 1.2 | 1.0 | 0.8 | 0.7 | 1.2 | 0.5 | 0.4 | 0.7 | 0.1 | 0.6 | 0.5 | 0.8 | 10.4 |
| 13.05.06 | 0.1 | 0.1 | 0.1 | 0.5 | 0.8 | 0.8 | 0.6 | 0.7 | 0.5 | 0.8 | 0.4 | 0.2 | 0.5 | 0.0 | 0.5 | 0.5 | 0.6 | 7.9 |
| 28.05.06 | 0.2 | 0.2 | 0.2 | 0.9 | 0.5 | 1.8 | 1.6 | 1.7 | 1.4 | 2.2 | 0.9 | 1.0 | 1.6 | 0.3 | 1.5 | 0.9 | 1.6 | 18.5 |
| 12.06.06 | 0.0 | 0.2 | 0.0 | 0.8 | 0.4 | 1.1 | 0.7 | 0.9 | 0.7 | 1.0 | 0.4 | 0.3 | 0.6 | 0.1 | 0.6 | 0.6 | 0.7 | 9.3 |
| 19.06.06 | 0.0 | 0.2 | 0.2 | 0.8 | 0.5 | 0.9 | 0.7 | 0.8 | 0.6 | 0.9 | 0.4 | 0.2 | 0.6 | 0.0 | 0.5 | 0.6 | 0.7 | 8.7 |
| 30.06.06 | 0.8 | 0.3 | 0.4 | 3.9 | 1.2 | 8.1 | 6.6 | 3.6 | 4.0 | 5.9 | 2.5 | 3.2 | 4.1 | 0.8 | 3.2 | 1.2 | 3.0 | 52.8 |
| 07.07.06 | 0.0 | 0.1 | 0.0 | 0.7 | 0.5 | 0.9 | 0.8 | 0.8 | 0.7 | 1.0 | 0.4 | 0.3 | 0.6 | 0.0 | 0.5 | 0.6 | 0.7 | 8.6 |

**Table E:** Results from the column test [ng L$^{-1}$]

| SV0 | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9.5. 12:00 - 10.5. 8:30 | 0 | 1 | 7 | 27 | 0 | 18 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10.5. 8:30 -22:45 | 1 | 3 | 5 | 14 | 1 | 5 | 3 | 2 | 5 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 10.5. 22:45 - 11.5.13:15 | 1 | 2 | 3 | 7 | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11.5. 13:15- 12.5. 9:00 | 1 | 2 | 3 | 8 | 1 | 2 | 2 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12.5. 9:00 - 13.5. 7:40 | 1 | 3 | 4 | 16 | 1 | 4 | 3 | 3 | 2 | 3 | 0 | 1 | 2 | 0 | 2 | 1 | 0 |
| 13.5. 7:40 - 15.5. 14:00 | 1 | 3 | 4 | 8 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 15.5. 14:00 - 16.5. 14:30 | 0 | 2 | 4 | 9 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 16.5. 14:30 - 17.5. 14:10 | 1 | 2 | 4 | 10 | 1 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 17.5. 14:10 - 18.5. 11:30 | 0 | 2 | 5 | 11 | 1 | 2 | 2 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 11:30 - 15:20 | 0 | 1 | 3 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 15:00 - 19.5. 12:00 | 1 | 2 | 4 | 11 | 1 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 19.5. 12:00 - 21.5. 16:00 | 1 | 2 | 4 | 9 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 21.5. 16:00 - 22.5. 13:00 | 1 | 2 | 5 | 11 | 1 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 0 |
| 22.5. 13:00 - 23.5. 15:30 | 0 | 0 | 143 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

| SV1 | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9.5. 12:00 - 10.5. 8:30 | 0 | 0 | 2 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10.5. 8:30 -22:45 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 10.5. 22:45 - 11.5.13:15 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11.5. 13:15- 12.5. 9:00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 12.5. 9:00 - 13.5. 7:40 | 0 | 0 | 4 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 13.5. 7:40 - 15.5. 14:00 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 15.5. 14:00 - 16.5. 14:30 | 0 | 0 | 2 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 16.5. 14:30 - 17.5. 14:10 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 17.5. 14:10 - 18.5. 11:30 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| 18.5. 11:30 - 15:20 | 0 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 15:00 - 19.5. 12:00 | 0 | 0 | 3 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 19.5. 12:00 - 21.5. 16:00 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 21.5. 16:00 - 22.5. 13:00 | 0 | 1 | 1 | 4 | 0 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 2 |
| 22.5. 13:00 - 23.5. 15:30 | 3 | 0 | 3 | 1 | 1 | 1 | 1 | 7 | 5 | 15 | 3 | 8 | 11 | 3 | 10 | 2 | 9 |

**Table E:** Results from the column test [ng $L^{-1}$]

| SV2 | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9.5. 12:00 - 10.5. 8:30 | 0 | 0 | 1 | 2 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10.5. 8:30 -22:45 | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 10.5. 22:45 - 11.5.13:15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11.5. 13:15- 12.5. 9:00 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 12.5. 9:00 - 13.5. 7:40 | 0 | 0 | 3 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 13.5. 7:40 - 15.5. 14:00 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 15.5. 14:00 - 16.5. 14:30 | 0 | 0 | 2 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 16.5. 14:30 - 17.5. 14:10 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 17.5. 14:10 - 18.5. 11:30 | 0 | 0 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 11:30 - 15:20 | 0 | 0 | 0 | 1 | 0 | 7 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 15:00 - 19.5. 12:00 | 0 | 0 | 4 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 19.5. 12:00 - 21.5. 16:00 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 21.5. 16:00 - 22.5. 13:00 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 22.5. 13:00 - 23.5. 15:30 | 2 | 0 | 3 | 0 | 0 | 1 | 1 | 4 | 3 | 9 | 1 | 5 | 6 | 2 | 6 | 2 | 5 |

| SV3 | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9.5. 12:00 - 10.5. 8:30 | 0 | 1 | 3 | 5 | 0 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10.5. 8:30 -22:45 | 0 | 1 | 3 | 3 | 0 | 2 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| 10.5. 22:45 - 11.5.13:15 | 0 | 1 | 1 | 2 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11.5. 13:15- 12.5. 9:00 | 0 | 1 | 2 | 3 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 12.5. 9:00 - 13.5. 7:40 | 0 | 2 | 3 | 3 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 13.5. 7:40 - 15.5. 14:00 | 1 | 2 | 3 | 5 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 15.5. 14:00 - 16.5. 14:30 | 0 | 2 | 3 | 4 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 16.5. 14:30 - 17.5. 14:10 | 0 | 2 | 3 | 5 | 0 | 3 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 17.5. 14:10 - 18.5. 11:30 | 0 | 2 | 4 | 5 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 11:30 - 15:20 | 0 | 1 | 2 | 5 | 1 | 2 | 1 | 2 | 1 | 2 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 15:00 - 19.5. 12:00 | 0 | 2 | 3 | 5 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 1 | 0 |
| 19.5. 12:00 - 21.5. 16:00 | 0 | 2 | 4 | 6 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| 21.5. 16:00 - 22.5. 13:00 | 0 | 2 | 4 | 5 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 |
| 22.5. 13:00 - 23.5. 15:30 | 3 | 2 | 4 | 5 | 1 | 1 | 1 | 4 | 3 | 10 | 2 | 5 | 7 | 2 | 7 | 2 | 6 |

**Table E:** Results from the column test [ng L$^{-1}$]

| SV4 | Any | Ace | Fln | Phe | Ant | Fth | Py | BaA | Chr | BbF | BkF | BeP | BaP | Per | Indo | DahA | BghiP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9.5. 12:00 - 10.5. 8:30 | 0 | 0 | 3 | 1 | 8 | 5 | 3 | 2 | 4 | 3 | 1 | 3 | 1 | 0 | 1 | 0 | 1 |
| 10.5. 8:30 -22:45 | 0 | 0 | 3 | 2 | 10 | 6 | 5 | 4 | 6 | 7 | 3 | 4 | 4 | 1 | 3 | 1 | 3 |
| 10.5. 22:45 - 11.5.13:15 | 0 | 0 | 2 | 1 | 8 | 3 | 2 | 2 | 3 | 2 | 1 | 2 | 1 | 0 | 1 | 0 | 1 |
| 11.5. 13:15- 12.5. 9:00 | 0 | 0 | 2 | 1 | 9 | 2 | 2 | 2 | 3 | 3 | 0 | 2 | 1 | 0 | 1 | 1 | 1 |
| 12.5. 9:00 - 13.5. 7:40 | 0 | 0 | 3 | 2 | 8 | 2 | 1 | 2 | 2 | 2 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 13.5. 7:40 - 15.5. 14:00 | 0 | 0 | 1 | 3 | 10 | 3 | 2 | 2 | 3 | 3 | 1 | 2 | 1 | 0 | 1 | 0 | 1 |
| 15.5. 14:00 - 16.5. 14:30 | 0 | 0 | 3 | 3 | 11 | 3 | 2 | 2 | 3 | 2 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 16.5. 14:30 - 17.5. 14:10 | 0 | 1 | 5 | 4 | 16 | 4 | 2 | 2 | 3 | 3 | 0 | 2 | 1 | 0 | 1 | 1 | 2 |
| 17.5. 14:10 - 18.5. 11:30 | 0 | 1 | 3 | 6 | 18 | 6 | 3 | 2 | 4 | 3 | 1 | 2 | 1 | 0 | 1 | 1 | 2 |
| 18.5. 11:30 - 15:20 | 0 | 1 | 3 | 3 | 8 | 3 | 2 | 2 | 2 | 2 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 18.5. 15:00 - 19.5. 12:00 | 0 | 1 | 3 | 3 | 12 | 3 | 2 | 2 | 3 | 3 | 0 | 1 | 1 | 0 | 1 | 1 | 2 |
| 19.5. 12:00 - 21.5. 16:00 | 0 | 1 | 2 | 4 | 12 | 4 | 2 | 2 | 3 | 3 | 1 | 2 | 1 | 0 | 1 | 1 | 1 |
| 21.5. 16:00 - 22.5. 13:00 | 0 | 1 | 2 | 4 | 13 | 3 | 2 | 2 | 3 | 2 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 22.5. 13:00 - 23.5. 15:30 | 7 | 1 | 1 | 4 | 13 | 4 | 3 | 6 | 7 | 18 | 3 | 11 | 10 | 3 | 13 | 3 | 12 |

**TABLE F-1:** Isotope signal of the precipitation.

| | $\partial^{18}$O | | $\partial^{18}$O | | $\partial^{18}$O |
|---|---|---|---|---|---|
| 05.03.05 | -5,7 | 16.09.05 | -9,4 | 04.03.06 | -22,4 |
| 22.03.05 | -9,8 | 29.09.05 | -6,6 | 05.03.06 | -24,6 |
| 22.05.05 | -6,5 | 01.10.05 | -7,9 | 07.03.06 | -10,0 |
| 04.06.05 | -5,9 | 02.10.05 | -8,0 | 08.03.06 | -11,9 |
| 16.06.05 | -9,3 | 03.10.05 | -7,8 | 09.03.06 | -9,5 |
| 01.07.05 | -8,5 | 04.10.05 | -6,9 | 10.03.06 | -9,1 |
| 04.07.05 | -9,3 | 02.11.05 | -7,2 | 12.03.06 | -17,9 |
| 08.07.05 | -7,7 | 04.11.05 | -11,4 | 13.03.06 | -16,2 |
| 11.07.05 | -7,7 | 21.11.05 | -14,9 | 21.03.06 | -9,3 |
| 18.07.05 | -2,9 | 16.12.05 | -9,2 | 26.03.06 | -7,6 |
| 18.07.05 | -2,6 | 17.12.05 | -10,7 | 28.03.06 | -8,6 |
| 24.07.05 | -9,0 | 27.12.05 | -11,6 | 31.03.06 | -7,5 |
| 25.07.05 | -8,3 | 29.12.05 | -17,3 | 05.04.06 | -10,4 |
| 02.08.05 | -3,8 | 31.12.05 | -16,2 | 10.04.06 | -16,8 |
| 02.08.05 | -3,6 | 08.02.06 | -10,5 | 17.04.06 | -5,6 |
| 19.08.05 | -4,8 | 09.02.06 | -11,3 | 25.04.06 | -7,2 |
| 21.08.05 | -7,2 | 10.02.06 | -15,4 | 27.04.06 | -8,4 |
| 22.08.05 | -8,5 | 11.02.06 | -13,5 | 09.05.06 | -11,2 |
| 25.08.05 | -7,6 | 26.02.06 | -15,3 | 13.05.06 | -5,6 |
| 02.09.05 | -6,1 | 01.03.06 | -17,7 | 16.05.06 | -8,5 |
| 10.09.05 | -7,5 | 02.03.06 | -12,9 | 16.05.06 | -5,1 |
| 12.09.05 | -10,7 | 03.03.06 | -16,7 | 18.05.06 | -4,6 |

**TABLE F-2:** Isotope signal of the cave seepage water (LTH).

| | ∂18O | | ∂18O | | ∂18O |
|---|---|---|---|---|---|
| 08.02.05 | -10,1 | 24.08.05 | -10,0 | 15.01.06 | -9,6 |
| 27.02.05 | -9,9 | 25.08.05 | -10,3 | 22.01.06 | -9,6 |
| 06.03.05 | -10,1 | 06.09.05 | -10,1 | 31.01.06 | -9,7 |
| 13.03.05 | -9,9 | 14.09.05 | -10,2 | 11.02.06 | -9,5 |
| 21.03.05 | -10,0 | 17.09.05 | -10,0 | 16.02.06 | -9,6 |
| 24.03.05 | -10,1 | 24.09.05 | -10,1 | 26.02.06 | -9,7 |
| 28.03.05 | -10,2 | 29.09.05 | -10,1 | 02.03.06 | -9,8 |
| 05.04.05 | -10,0 | 15.10.05 | -10,1 | 10.03.06 | -9,7 |
| 09.04.05 | -10,2 | 21.10.05 | -10,1 | 16.03.06 | -9,9 |
| 19.04.05 | -10,0 | 28.10.05 | -10,3 | 28.03.06 | -10,6 |
| 25.04.05 | -9,6 | 11.11.05 | -10,1 | 30.03.06 | -10,6 |
| 06.05.05 | -10,0 | 20.11.05 | -10,1 | 04.04.06 | -10,2 |
| 11.05.05 | -9,9 | 27.11.05 | -10,1 | 04.04.06 | -10,0 |
| 13.05.05 | -9,8 | 27.11.05 | -10,2 | 12.04.06 | -10,0 |
| 25.05.05 | -9,8 | 27.11.05 | -9,9 | 19.04.06 | -9,9 |
| 18.06.05 | -9,9 | 29.11.05 | -9,9 | 26.04.06 | -9,9 |
| 25.06.05 | -10,1 | 01.12.05 | -10,1 | 30.04.06 | -10,0 |
| 08.07.05 | -10,1 | 11.12.05 | -9,9 | 09.05.06 | -10,2 |
| 27.07.05 | -10,2 | 18.12.05 | -9,9 | 09.05.06 | -9,9 |
| 14.08.05 | -10,1 | 08.01.06 | -9,8 | 13.05.06 | -10,3 |

**TABLE F-3:** Isotope signal of the cave seepage water (NS and VH).

| | ∂$^{18}$O (NS) | ∂$^{18}$O (VH) |
|---|---|---|
| 11.11.05 | -10,2 | -9,3 |
| 20.11.05 | -9,8 | -9,9 |
| 01.12.05 | -9,2 | -10,0 |
| 11.12.05 | -9,8 | -10,0 |
| 18.12.05 | -9,9 | -10,1 |
| 29.12.05 | -9,7 | -9,8 |
| 08.01.06 | -10,0 | -9,8 |
| 15.01.06 | -9,6 | -10,0 |
| 22.01.06 | -9,9 | -9,9 |
| 31.01.06 | -9,8 | -9,5 |
| 11.02.06 | -9,6 | -9,4 |
| 16.02.06 | -9,8 | -9,7 |
| 19.02.06 | -9,9 | -9,8 |
| 26.02.06 | -9,7 | -9,7 |
| 02.03.06 | -9,6 | -9,9 |
| 10.03.06 | -9,7 | -10,1 |
| 16.03.06 | -9,8 | -10,0 |
| 23.03.06 | -9,8 | -9,8 |
| 28.03.06 | -9,9 | -10,4 |
| 30.03.06 | -10,6 | -10,2 |
| 04.04.06 | -9,8 | -9,9 |
| 12.04.06 | -9,9 | -10,2 |
| 19.04.06 | -9,8 | -10,4 |
| 30.04.06 | -10,2 | -10,3 |
| 09.05.06 | -9,9 | -10,5 |
| 13.05.06 | -9,9 | -10,3 |

**TABLE F-4:** Isotope signal of the groundwater (BT).

| | ∂18O |
|---|---|
| 06.03.05 | -10,0 |
| 18.03.05 | -9,9 |
| 20.03.05 | -9,9 |
| 21.03.05 | -9,8 |
| 23.03.05 | -10,0 |
| 29.03.05 | -10,0 |
| 23.04.05 | -10,5 |
| 25.05.05 | -9,9 |
| 25.05.05 | -9,7 |
| 18.06.05 | -9,8 |
| 06.07.05 | -9,8 |
| 06.07.05 | -9,8 |
| 25.07.05 | -10,0 |
| 21.08.05 | -9,7 |
| 25.09.05 | -9,9 |
| 05.10.05 | -9,6 |
| 29.10.05 | -9,8 |
| 19.11.05 | -10,1 |
| 01.12.05 | -10,0 |
| 30.12.05 | -10,0 |
| 21.01.06 | -9,9 |
| 17.02.06 | -10,0 |
| 30.03.06 | -10,5 |
| 31.03.06 | -10,5 |
| 21.04.06 | -9,9 |
| 13.05.06 | -9,8 |

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