Spatial, Temporal, and Inter-compartmental Environmental Monitoring of Lipophilic Pollutants by Virtual Organisms

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**ABSTRACT**

Sampling points belonging to the Harz National Park river system, Germany, were selected between the period of 2014 and 2017 for monitoring polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in water, air, and sediment. Triolein-containing Virtual Organisms (VO) were employed to assess the levels of chemicals in water, air and triolein as surrogate for natural fat. To avoid overestimation of the concentrations 20 performance reference compounds (PRCs)-16 PRCs-PAHs and 4 PRCs-PCBs were covering the range of properties of native compounds. Results manifested the highest concentration of individual PAH as follows: 31 ng fluoranthene/L water, 3600 ng pyrene/g fat, 62 ng phenanthrene/m3 air and 2800 ng fluoranthene/g dw sediment. All PCBs and OCPs values were below above mentioned PAH concentrations and far below EU-limit levels. Environmental partition of chemicals was investigated by calculating fugacity, suggesting a mass transport from water to air. Only quite volatile compounds such as hexachlorobutadiene showed higher fugacity in air. Ratios of sediment/water concentrations and log Kow within individual sampling periods at Holtemme River exhibited strong linear relationships. Interestingly, during summer months of the years water and fat contents well correlate to the flow rates of Holtemme River. Our results show that VO can be successfully used as a tool for ongoing exposure assessment studies and predictions of worst case levels in food and nutrition.

1. **Introduction**

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) entering the natural ecosystems are distributed into solid, liquid, or gaseous phases within environmental compartments. Despite the regulation of these substances, they are still detected in the environment because of their relatively low water solubility, vapor pressure, and relatively large octanol-water and octanol-air partition coefficients (Omwoma et al., 2019). It has been for long time assumed that food consumption is the main source for PCB bioaccumulation in human, however recently was estimated that inhalation of PCBs can have also an important contribution to the human exposure (Norström et al. 2010; Heiger-Bernays et al., 2020). Since 4,4′-DDT degrades to 4,4′-DDE and 4,4′-DDD these substances may be remobilized from contaminated soils or sediments (Bandow et al., 2020). PAHs are emitted into the atmosphere from various combustion sources including automotive combustion engines (Mi et al., 2000) and small wood stoves/boilers used for domestic heating (Fernandes and Brooks, 2003; Bari et al., 2010). They are also released into the aquatic environment through the discharges from human activities such as industrial and domestic sewage effluents (Zhai et al., 2011). In addition, it is well recognized that these contaminants are widely distributed all over the globe and subsequent atmospheric transport and temperature-dependent partitioning between the atmosphere and environmental media is a leading pathway for their diffusion (Lohmann et al., 2007; Nizzetto et al., 2010). On the other hand, in the Arctic these persistent organic pollutants (POPs), deposited into typical sinks such as soil and ice, are expected to revolatilize into the atmosphere, and there is evidence that this revolatilization process may have already begun (Ma et al., 2011).

Consequently, PAHs, PCBs and OCPs may cause adverse human health effects even far away from their origin. It is known that organisms can bioaccumulate low to relatively high levels of such contaminants in their lipids. In recent years, Virtual Organisms (VO) (Schramm et al., 2013) have been successfully used for determinations of POPs in water, sediments, and air (Amdany et al., 2014; Temoka et al., 2016; Zhu et al., 2013) due to their attractive properties (i.e. their long-term stability, low cost, and ease of deployment). Semipermeable membrane devices (SPMD) containing performance reference compounds (PRCs) are the most common devices for analysis of pollutants in water. In this study, the VO is recognized as a type of SPMD. Theoretically, the kinetics of PRCs spiked into the passive sampler are used to estimate the site-specific sampling rates of the chemicals for each SPMD and the rates of PRC losses are proportional to the rates of analyte uptake (Karacik et al., 2013). The method was first introduced by Huckins et al. (2002, 2006), and recently Booij and Smedes (2010) and Temoka et al. (2016) suggested an improved method for estimation of OCP sampling rates in aquatic samples. However, Temoka et al. (2016) suggested the use of field data for the calculation of sampling volume in order to avoid overestimation of the water concentration. Altogether, only limited data pertaining to the use of these passive smpling tools using SPMDs in layflat-low-density polyethylene (LDPE) tuning for air monitoring is available in the literature (Ockenden et al., 2001; Zhu et al., 2013; Booij and van Drooge, 2001; Prest and Jacobson, 1995).

In this study, the levels of PAHs, PCBs and OCPs were determined for the first time in parallel in the aquatic and atmospheric environment, with triolein-containing VOs at a higher amount, to improve the LOQs. Triolein is a symmetrical triglyceride and also known surrogate of natural fat, derived from glycerol and three units of the unsaturated fatty acid oleic acid. Since triolein is a main component of olive oil and has a large amount of oleic acid (Hares Junior et al., 2018), it has been studied in different investigations on nutrition (Hassett, 2004; Chapagain and Wiesman, 2009)and widely used as the ingredients in cosmetics (Ting et al., 2019).

VOs utilized as passive samplers for the contaminants in water and air and total air (air + aerosols) concentrations were estimated. In addition, sediment concentrations were investigated. In our study the abundance of PAHs, PCBs and OCPs according to sampling location, pattern analysis, and comparison to guideline values are further discussed. The riverine system and its tributaries in the area of the Harz National Park were selected to examine the fate, transport and risk of the three categories of substances in different seasons between 2014 and 2017.

1. **Materials and Methods**
   1. **VO sampler preparation**

The procedure for triolein-containing-VO sampler preparation in this study was similar to that described by Wang et al. (2009). In brief, low-density polyethylene lay flat tubings (LDPE, 2.5 cm wide, wall thickness 65 µm; VWR Ismaning, Germany) were used. The LPDE tube was heat-sealed at a distance of 2.5 cm from one end. To increase the accumulative power of the VO compared to SPMD, 700 µL of triolein (Sigma, Munich, Germany, 99%) spiked with performance reference compounds (PRC) were added as close as possible to the sealed bottom by using a capillary pipette. The PRC compounds were: Naphthalene-13C6, Acenaphthylene-13C6,Acenaphthene-13C6,Fluorene-13C6, Phenanthrene-13C6, Anthracene-13C6, Fluoranthene-13C6, Pyrene-13C3, Benz(a)anthracene-13C6,Chrysene-13C6, Benzo(b)fluoranthene-13C6, Benzo(k)fluoranthene-13C6, Benzo(a)pyrene-13C4,Indeno(1,2,3-cd)pyrene-13C6, Benzo(ghi)perylene-13C12, Dibenz(a,h)anthracene-13C6, 13C12-PCB37, -PCB60, -PCB127, -PCB159). The length of the whole VO was 29 cm and the triolein-containing part of the sampler (i.e., excluding the mounting loops) had an area of 115 cm2. The sampler preparation was performed in a purified glovebox under nitrogen atmosphere to avoid contaminations. The prepared VO were stored in 20 mL glass vials capped with heat-sealed aluminium foil and stored at -28 oC until deployment in the field.

* 1. **Field Sampling**

Sampling was conducted within the Harz Mountain Range and the Harz Lowland (German federal states of Lower Saxony and Saxony-Anhalt), parts of which belong to the Harz National Park that is part of Natura 2000 – the European nature conservation network. Because of its geographical location and beautiful landscape, approximately 10 million visitors per year are registered in the Harz National Park area. Most creeks and rivers within this area belong to the Bode River catchment. Selke River is a right-hand tributary of the Bode River, which starts in the Harz Mountains and breaks out at the north-eastern Harz Lowland of Saxony-Anhalt, Germany (location Meisdorf) (Fig. 1). The Holtemme River with a catchment of 278 km2 is another river that drains into the Bode River and flows through several rocky cascades as “Steinerne Renne” (“stony run”), a relative fast flowing section (Karthe et al., 2017). Further, the Holtemme River passes through Wernigerode whose sections are channelized with dams. There are two gauging stations along the investigated Holtemme River, one located at Steinerne Renne (41 km from basin outlet) and another one located at Mahndorf (19.3 km from basin outlet). These gauging stations were chosen because of sampling availability and safety of samples over the long periods of deployment.

Fig. 1

The sediment samples were collected from the inside of the VO-container in which sediment particles less than 1 mm regularly deposit during the sampling periods from four different sampling points located near Meisdorf (Selke River), Steinerne Renne, Nienhagen (Holtemme River River), and Drei Annen Hohne (Wormsgraben creek) during October 2014 until October 2017 (Table 1S). In addition, the VO was exposed in cages in water and air (light protected) for a minimum of 15 d to a maximum of 156 d at seven field sites across the Bode River catchment during May 2014 until October 2017 (Table 1S). The variations of the sampling intervals were determined by logistical parameters such as availability of the location along events such as flood water, seasoning like winter and heavy snow fall and personnel disposition. Due to the theory of VO data can be harmonized by PRC for different sampling times. For water monitoring, the sampling sites were: Meisdorf, river gauge of Selke River, Meisdorf, river bed of Selke River, Nienhagen, river bed of Holtemme River, Wernigerode, stream Steinerne Renne, Drei Annen Hohne, Wormsgraben creek. For air monitoring the sampling sites were on the roof of MOBICOS research stations (Fink et al., 2020) at Nienhagen and Wormsgraben.

The VO were exposed in stainless steel cages and submerged under water above the sediment. The flow rates of Holtemme River at Mahndorf near Nienhagen, Steinerne Renne at Wernigerode, and Selke River at Meisdorf are presented in Figures 1S-3S. The sampling periods, the mean flow rates (m3/s) of Holtemme River and the identified groups of “summer” (sampling period from May to November) and “winter” (sampling period from November to May) months of the year are shown on Table 2S. Exclusively high mean flow rate of 1.66 m3/s was observed during May-November 2017. This sample was excluded in the discussions of results in regard to seasonal relationships.

After the deployment period, the corresponding VO were removed from the cages, encased in their original glass vials and stored at−28°C until sample preparation and analysis.

* 1. **Studied compounds**

This study focused on indicator PCBs (namely PCB #28, PCB #52, PCB #101, PCB #138, PCB #153, and PCB #180), non-ortho-, and mono-ortho-PCBs. Thirty (30) organochlorine compounds and one pyrethroid were also studied, specifically: α-, β-, γ-, δ-, and ε-hexachlorocyclohexane (HCH), hexachlorobutadiene (HeCBD), pentachlorobenzene (PeCB), hexachlorobenzene (HCB), pentachloroanisole (PCA), octachlorostyrene (OCS), isomers of DDT, DDE, and DDD (namely 4,4’- , 2,4’-DDT, 4,4’- , 2,4’-DDE, and 4,4’- , 2,4’-DDD), trans-, cis-, and oxy-chlordane (CLH), heptachlor (HC), cis- and trans-heptachlor epoxide (HCE), aldrin, dieldrin, endrin, α- and β-endosulfan (Endo), endosulfan-sulfate (Endo-sulfate), mirex and cypermethrin. This list was extended with the 16 priority U.S. Environmental Protection Agency (EPA) PAHs, namely naphthalene (NA), acenaphthylene (ACL), acenaphthene (AC), fluorene (FL), phenanthrene (PHE), anthracene (AN), fluoranthene (FA), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbFA), benzo[k]fluoranthene (BkFA), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (IP), benzo[g,h,i]perylene (BghiP), and dibenzo[a,h]anthracene (DBahA).

* 1. **Extraction, clean-up and analysis**

The samples (VO samplers and sediments) were spiked prior extraction with a range of deuterated and 13C-labeled compounds (deuterated 16 EPA PAH mix and 13C-labeled mix of OCP and PCB, see Table 3S and 4S) for quantification and as efficiency controls for extraction and cleanup procedures. 10 g of lyophylized sediment samples were extracted by Accelerated Solvent Extraction System (Dionex ASC 200) with a mixture of extraction solvents n-hexane/acetone (3:1 v/v). The VO were cross-checked for tightness and weight, carefully rinsed outside with deionized water and then cut into small pieces before extraction with 100 mL cyclohexane in a glass volumetric flask overnight at 200 rpm on a constant left-right shaker. The volumes of generated extracts for both sediment and VO- samples were reduced to 1mL and the residues were redissolved again with approximately 1-2 mL mixture of n-hexane:dichloromethane (1:1). Subsequently, each sample underwent a two-step cleanup, first using a mixed column containing silica and alumina, second a C18 SPE cartridge (Wang et al., 2015). Recovery standards (13C12-1,2,3,4-TCDD, Pentachlorotoluene, 13C12-1,2,3,7,8,9-HxCDD, 13C12-PCB70, 111, and 170) were added in the final eluate and the resultant sample was concentrated with a gentle flow of nitrogen to 20 µL to be ready for analytical determination.The analysis was carried out with HRGC/HRMS. The parameters used for the isomer specific detection of PAHs, PCBs and OCPs are given in Temoka et al. (2016) and Wang et al. (2015). All results were expressed as pg/VO or pg/g dry weight basis (d.w.) for sediment, respectively, and those analytes with concentrations less than the detection limits are reported as not detected (n.d.).

* 1. **Quality control/quality assurance**

The accredited laboratory applied quality management system practices according to EN ISO/IEC 17025 standards. The applied analytical methods are regularly verified in interlaboratory comparison studies.

For sediments 10 procedural blanks and for VOs 17 field blanks were analysed. All used solvents, silica, and alumina adsorbents were of trace analysis grade and supplied by LGC Standards (Wesel, Germany). The field VO blanks were carried to and from the place of deployment, and after being briefly opened at the deployment place, hermetically sealed and then stored at -28 °C at the laboratory for the same period as the VO sampling deployment. The generated data were blank-corrected as an average of all field blanks values were subtracted from the sample values. Analytes whose concentrations after blank correction were lower than three times the standard deviation of the field blank values were considered as not detectable (n.d.) and their result was considered as zero for the further calculations regarding water and air samples. Results of the sediment samples were corrected for blanks by the same procedure using the mean and standard deviation of the procedural blanks. Analytes in samples that were not detected before field blank correction were given also as not detectable (n.d.). The limit of quantification (LOQ) of the instrumental methodology was considered as a signal/noise ratio of 9:1. The levels of LOQ, field or laboratory blanks and the percentage of recovery of the labeled quantification standards are listed in Table 3S and 4S.

The PAHs, PCBs and OCPs compounds found in blanks with abundant concentrations were naphthalene (31 ng/VO), PCB#153 (458 pg/VO) and γ-HCH (267 pg/VO), respectively. The compounds with elevated LOQs were indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene (220 pg/VO), PCB#28 (23 pg/VO) and cypermethrin (216 pg/VO).

* 1. **Performance of PRC**

PRC are 13C labeled chemical identities of PAH and PCB which behave chemically identical to the native analogues besides of slight differences in their molecular weight which is taken into account as well. For OCP the relation between the log Kow \* molecular weight (MW) (Temoka 2017b) is correlated as best possible approach with the actual sampling rates Rs for PAH and PCB of each campaign. The correlation is then used to calculate the sampling rates of the OCP by introducing their MW and Kow.

PRC percentages of recovery after deployment in water and air are shown in Table 5S and 6S, respectively. It can be clearly seen that there are strong relations to chemical identity as well as to some extend also to seasons, especially for air which is most likely mainly related to the temperature dependence of the partition coefficient between water and air versus VO (Booij & Drooge 2001). However, the relation to the chemical identity is much stronger and crucial for a proper estimation of the native analytes to be determined.

The in situ sampling rates (Rs) values listed in Table 7S and 8S are underpinning the strong relation of Rs and chemical properties such as Kow and MW. The use of only one or two PRCs as often reported will lead to overestimation of the free water and air concentrations by orders of magnitude. Therefore, a set of chemicals covering at least the property range of the native compounds of interest is shown to be essential.

The percentages of equilibrium are presented in Table 9S and 10S for water and air and are complementary to the findings of Rs etc. A strong relation to chemical properties (Kow, MW) become visible. As expected compounds with low Rs are generally closer to equilibrium. However, for air the equilibria are closer to 100% than for water in most cases.

For some PRC-compounds, in particular the anthracene like compounds and benzo[a]pyrene in air, chemical reactions are indicated as additional factor of their specific performance as PRC because their ke- respectively Rs-values are higher and deviating from the pure chemical reaction to their Kow and MW (Calculation 1S, Table 8S). However, the strongest impact to final estimated concentrations are neither based on status to equilibrium nor percentage of losses.

The inclusion of a large set of PRCs reveals the main bias in using PRCs is the large range of real world Rs, which has to be taken into account more thoroughly for future investigations.

* 1. **VO data calculation for water and air samples**

The in situ sampling rates (Rs, PRC) of 16 PRC-13C-PAH and –PCB retained in VO and the log Kow (Temoka 2017b) were used to calculate the target analyte sampling rates Rsanalyte of various organic pollutants like PAHs, PCBs and OCPs and accurate values of water concentrations according to Temoka et al. (2016).

In addition, VO were utilized as passive samplers for the three categories of substances in air and air + aerosols based on the theory described by Huckins et al. (2006) for the sampling rate. The gas-concentrations were estimated based on the performance of the reference compounds, which were used to estimate the corresponding sampling volumes over the deployment period (Ockenden et al., 2001). The theory was finally improved by Temoka et al. (2016, 2017)for in situ reference compounds (13C labeled PAH and PCB) to calculate sampling rates on the basis of the on-site performance of the VO.

Here Ktrio\_air was obtained by calculating Ktrio\_water/(H/R T) with H (Pa m3 mol-1) (Temoka 2017b), R 8.3143 (Pa m3 mol-1 K-1) and T=293 K for the triolein part of the VO and K\_LPDEwater/(H/R T) with H (Pa m3 mol-1), R = 8.3143 (Pa m3 mol-1 K-1) and T=293 K as KLPDE\_air for the low density polyethylene membrane part of the VO. The KVO\_air can then be calculated as

KVO\_air = (Ktrio\_air Vtrio + KLPDE\_airVLPDE)/(Vtrio+VLPDE)

thus considering VO as a two compartment sampler consisting of accumulative volumes V of LPDE and V of triolein with their partition coefficients against air Ktrio\_air andKLPDE\_air. Ktrio\_water andKLPDE\_water were calculated according to Temoka et al. (2016) using empirical correlations between triolein and LPDE versus Kow.

The total air concentrations were calculated by using K\_aerosol-gas (Mackay at al., 1986) and summing the gaseous and aerosol part per m3 assuming an average aerosol concentration of 10 µg/ m3.

Fat (worst case) concentrations are calculated assuming equilibrium between the pure air and water versus triolein based on Ktrio\_air and Ktrio\_water  at a density of triolein of 0.95 kg L-1, thus being converted to mass/mass.

* 1. **Calculation of ratios within environmental compartments and their relation to physicochemical properties of the analytes**

For the calculation of the air/water and sediment/water ratios the raw water concentrations were initially converted to mass/m3 for air and water and mass/g for sediment in order to operate dimensionless ratios between air and water and comparing the ratios either to log Kow for sediment or to the dimensionless Henry constant for water. The logarithmic values of the resultant ratios were further calculated, and these values were correlated to the physicochemical constants, log Henry and log Kow (Table 11S and Table 12S). The determined linear coefficients (R2) of the correlated data were used to assess the equilibria of individual compounds for comparing the magnitudes of the deposition and volatilization ﬂuxes.

* 1. **Calculation of fugacities**

If the fugacities of a chemical in both compartments pure air f\_air and pure water f\_water (this is what the VOs are reflecting) are equal, the compartments are in equilibrium. If f\_air > f\_water mass transport occurs from air to water and if f\_air<f\_water mass transport direction is reversed. The fugacities are calculated as follows

f\_air = c\_air (mol m-3) R (Pa m3 mol-1 K-1) T (K) with R=8.3143 and T=293 K

f\_water = c\_water (mol m-3) H (Pa m3 mol-1) with H at T=293 K

1. **Results and Discussion**

The calculated PAH (ng/g fat, ng/L, g/day, ng/m3), PCB and OCP (pg/g fat, pg/L,mg/day, ng/m3, pg/m3) concentrations in water and air samples for the investigated locations are presented in Table 13S-20S. The PAH (ng/g dw), PCB and OCP concentrations (pg/g dw) in sediments are further shown in Table 21S-23S. The objectives of these data were to study the POPs distribution within environmental compartments in relation to corresponding physicochemical properties, water flow rate and season.

* 1. **Spatial distribution of the POPs in various environmental media of the Harz region**

*Water*

The PAH results (ng/L) exhibited that the dominant PAHs in the sampling locations were fluoranthene, phenanthren, pyren and fluorene (3 and 4 rings). The average percentage PAH homologue distribution suggested different PAHs pattern of the sampling locations as for Nienhagen: FA>Phe>PY>FL; for Meisdorf: FA~Phe >FL~AC~PY; for Steinerne Renne: FA> Phe>PY; for Drei Annen Hohne: FA~Phe>PY>FL (Figure 2).

Figure 2

However, a different PAH congener pattern was also observed for the calculated concentrations in ng/g fat for the investigated locations. For example, for the samples collected from Meisdorf and Nienhagen, the dominant PAHs were FA>PY>Phe, while for the sampling points at Drei Annen Hohne and Steinerne Renne, the distribution of the highest PAH levels was FA≈PY≈Chr≈BbFA (Figure 2). Considering these 4 sampling locations the highest levels ranging from 1.3-31 ng/L and 195-3600 ng/g fat were determined in Nienhagen and for the two nearby locations of Meisdorf, at bed and gauge of Selke River, similar concentrations ranging from 1-20 ng/L and 120-1730 ng/g fat were observed. The lowest values of 0.03-1.7 ng/L and 11-143 ng/g fat were determined at the sampling sites Drei Annen Hohne and Steinerne Renne. These two locations mainly receive atmospheric deposition of PAHs. Our results for benzo[a]pyrene in pure water concentration were low and did not exceed 0.024 ng/L, far below the guideline value of 0.7 µg/L for drinking water (WHO, 1996). Furthermore, our data was lower than the reported values of 0.025 µg/L and 0.017 µg/L BaP in rivers between 2015 and 2019 by the British Environmental Agency (Chemical Investigations Programme), respectively (EEA, 2019) and the environmental quality standard for BaP of 0.05 µg/L as annual average (UBA, 2016).

The limit of benzo(a)pyrene in oils and fats (excluding cocoa butter and coconut oil) intended for direct human consumption or use as an ingredient in food is 2 μg/kg (EC, 2011). Whereas it is for the sum of benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene and chrysene in oils and fats (excluding cocoa butter and coconut oil) intended for direct human consumption or use as an ingredient in food 10 μg/kg (EC, 2011). All existing limits for PAH in water were not exceeded (WHO, 2011), but in fat the current values were exceeding the fat limits. Since the estimation of fat concentration was based on conservatives assumptions, such as missing metabolism etc., this might be the reason for exceedance of limit values in fat.

Regarding the PCB levels (pg/L) in water samples, a pattern of distribution for the most water soluble congeners, PCB28>PCB52>PCB101 was observed. In general, many n.d. or low PCB values were identified in the samples. Similar to the PAH findings, the highest PCB amounts (max PCB28 value of 14.1 pg /L) were calculated for the sampling location at Nienhagen of Holtemme River and the lowest PCB amounts ranging from 0-1.9 pg/L were determined at the sampling sites Drei Annen Hohne and Steinerne Renne. However, an extraordinary PCB28 value of 4.3 pg /L was observed in the period of spring/summer 2016 in Steinerne Renne. Consequently, this particular result of PCB28 was in the same range as those obtained at the two locations at Selke River, Meisdorf. Since the United States Environmental Protection Agency (USEPA, 2009) set a maximum contaminant level of 500 ng /L for PCBs in drinking water, it can be concluded that the PCB water concentrations in our investigations are very low.

Another PCB pattern was found when the concentrations were expressed in pg/g fat. For these results the dominant congeners were PCB153 and PCB138 and the maximum value obtained was about 10 ng/g fat for PCB138 for the water samples of Holtemme River. The highest concentrations in the range of 5.6 - 8.6 ng/g fat were determined for PCB153 in Meisdorf, at sampling locations in Selke River and Steinerne Renne, while in Drei Annen Hohne the highest level was 3.6 ng/g fat (PCB153).

The potential dl-PCB TEQ values for human and animal-like fat in the different sampling locations were calculated. For the two sampling locations of Meisdorf and Holtemme the results were in the range of 2.8-4.3 pg TEQ2005/g fat (excluding the samples presented with mainly n.d. and zero PCB TEQ values, respectively which were observed mainly in Meisdorf area). A maximum value of 10.35 pg TEQ2005/g fat was obtained from samples taken during the period from 30.01.-09.05.2017 in Nienhagen in the bed of Holtemme River. Negligible dl-PCB TEQ results were determined for the samples collected at Drei Annen Hohne and Steinerne Renne.

In current regulations the following limits are set as. Sum PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180 in marine oils (fish body oil, fish liver oil and oils of other marine organisms intended for human consumption) is 200 ng/g fat (EC, 2011). All existing limits for PCB are not exceeded.

The concentrations (pg/L) in water of the individual OCPs were generally below the value of 100 pg/L with exception of γ-HCH whose concentrations were in the range of 100-500 pg/L detected in samples of Nienhagen, Holtemme River. Furthermore, at the same location, a maximum value of 658 pg α-HCH /L was found during the period from May to October 2017. Taking into account the maximum contaminant level (MCL) of 0.1 μg/L for individual OCPs and 0.5 μg/L for total OCPs concentrations, as cited in the European Union (EC, 2013) all the values obtained for OCPs in this study were far below corresponding EU limit-levels.

Regarding OCP concentrations expressed per unit of fat, the maximum result was 75 ng/g fat obtained for 4,4’-DDD in Selke River (Meisdorf). In both Meisdorf locations such high values were found and the dominant compounds were 4,4’-DDD>4,4’-DDE>2,4’-DDD with concentrations ranging from 0.6-69 ng/g fat. The levels of the rest of the OCPs were below 10 ng/g fat. For the samples collected in Holtemme River the dominant two compounds were 4,4'-DDE> 4,4’-DDD>2,4’-DDD, with concentrations ranging from 0.2-56 ng/g fat, whereas the other OCP compounds were not above 19 μg/g fat. For the water samples collected in Drei Annen Hohne and Steinerne Renne the dominant compounds were 4,4’-DDE (max value of 24 ng/g fat) >4,4’-DDT and 4,4’-DDE (max value of 55 ng/g fat) >4,4'-DDD~4,4'-DDT, respectively. The elevated DDT concentrations might be explained by that fact, that the investigated Harz region belonged to the former German Democratic Republic (GDR) of Germany characterized with regional pollution of soil (Pandelova et al., 2018; Berger and Schwarzbauer, 2016), surface water and ground water (Wycisk et al., 2003) due to intensive spraying of DDT against bark beetle in the 1980s in this area.

The mass transfer over the total observation period was studied for PAH, PCB, and OCP on the basis of mass/day, respectively. Since in Wormsgraben no gauge existed, the total runoff during sampling periods was not available and the mass/day could not be reported in Table 17S. In general, the results of the other sampling locations as Meisdorf, Steinerne Renne and Nienhagen (Table 13-16S) followed the same pattern distribution as the above mentioned results on liquid and fat basis for the investigated three categories of contaminants. During the entire sampling period some escalated mass/day values were identified but they were found to fluctuate within sampling locations and contaminant category. For example, in Holtemme River about 3 g/day phenanthrene and fluoranthene each were detected in October 2014-February 2015, 1 mg/day PCB 28 was detected in May-July 2016, 71 mg/day γ-HCH, 5 mg/day HCB and 7 mg/day 2,4’-DDD were detected in May-October 2017. Within 10- and 100- times lower mass/day values were reported in rivers Steinerne Renne than in Holtemme. For example, the highest levels of phenanthrene and fluoranthene were 0.03 g/day each within the whole sampling period of 2015-2017, 0.05 mg/day PCB 28 was detected in May-July 2016, 0.6 mg/day HCB in May-August 2017, 0.3 mg/day 4,4’-DDT in July-November 2016, 2.6 mg/day and 2.2 mg/day 4,4’-DDT and 4,4’-DDD, respectively were detected in May-August 2017. No detected values were found for γ-HCH during the whole sampling periods in river Steinerne Renne.

At sampling location of Selke extraordinary high values were determined, e.g. 1.5 g/day phenanthrene during November 2014-February 2015, and 0.3 mg/day PCB28 during June-October 2014, 6.5 mg/day and 6 mg/day γ-HCH and 4,4’-DDD in June-October 2014, respectively.

The relationships between the sums of the daily mass transfers and the flow rates (m3/s) (Fig. 3) in the riverine system for the sampling periods were studied additionally. Significant correlation was only found for the samples collected from river Steinerne Renne. Figure 3 shows this relationship by presenting the sum of the daily mass transfer and the flow rate (m3/s) of the riverine system Steinerne Renne.

Fig. 3

*Air samples*

Four dominant compounds, namely phenanthrene≈fluorene > acenaphthylene≈acenaphthene (3 rings) within PAH (ng/m3) group were found in Nienhagen, Drei Annen Hohne and Steinerne Renne, with total (gaseous and aerosol part) concentrations ranging from 0 to 62 ng/m3 (Table 18-20S). Profound levels of phenanthrene and fluorene were determined in “summer” and “winter” periods of the year. The highest concentration of 62 ng phenanthrene/m3 was reported during the sampling period of November 2016-January 2017. The same finding was also observed for the ng/g fat results, but in this case the levels of phenanthrene were much higher than fluorene. Negligible concentrations were reported for benzo(a)pyrene and the data was below the EU target value of 1 ng/m3 (EEA, 2019). Mainly not detected PCB concentrations were reported in the air samples collected from Drei Annen Hohne and Steinerne Renne. For the samples collected in Nienhagen the indicator – PCBs (PCB-28, -52, -101, -138, -153) were determined in concentrations of 0 to 36 pg/m3 and 0 to 1150 pg/g fat and all other congeners were reported with values of zero. However, exceptionally fat contents of 1120 pg PCB#28/g fat and 1150 pg PCB#153/g fat were reported in Nienhagen during May-July 2016 and October-December 2014, respectively. Regarding OCPs, a tendency of higher amounts for Cl6butadiene, Cl5benzene, Cl5anisole, Cl8styrene (up to 6000 pg/m3 for Cl6butadiene in Nienhagen during August-October 2017 and up to 9000 pg/g fat for Cl6benzene in Nienhagen during December 2014 and February 2015) was found in all samples collected. Moreover, 4,4'-DDT, 2,4'-DDT, 4,4'-DDE and 2,4'-DDE were identified with sustainable concentrations within 17 and 15500 pg/g fat and 0 and 28 pg/m3 in Nienhagen samples (the highest values are identified for 4,4'-DDT during May-August 2017).

*Surface sediment samples*

Three of the dominant PAHs in water samples were also found abundantly in surface sediments as fluoranthene> pyren> phenanthrene (3 and 4 rings) (Table 21S-23S). The highest value of 2800 ng fluoranthene /g dw was reported for Nienhagen. In general, the results at this sampling location were about three and six times higher than those found in Meisdorf and Drei Annen Hohne, respectively.

PCB pattern as PCB 28> PCB 52 > PCB 180 was observed for samples collected in Meisdorf and Drei Annen Hohne. However, interestingly a different pattern as PCB 138≈PCB 153 >PCB 180 was observed for the samples collected in Holtemme River. In contrast to the PAH results, the maximum PCB concentrations were determined in the samples collected in Meisdorf (19 ng PCB#153/g dw) followed by the samples collected in Nienhagen (6 ng PCB#138/g dw). In general, these values did not exceed the reported (UBA, 2018) annual averages of <0.4-389 µg/kg of PCBs in suspended soils/sediment regarding the monitoring of 2014-2016 in Germany. The OCP pattern in sediment samples in Meisdorf was similar to the pattern for water samples as: 4,4’-DDD (max value of 9 ng/g dw)>4,4’-DDE≈ 2,4’-DDT (max value of 6 ng/g dw). For the sediment samples in Nienhagen the dominant OCPs were 4,4’-DDE≈4,4'-DDT (max value of about 16 ng/g dw) > 4,4’-DDD ≈Cl6benzene (max value of 8 ng/g dw) however, all other OCPs were found below 2 ng/g dw. The highest value determined in Drei Annen Hohne area was 13 ng/g dw for 4,4’-DDD followed by 6 ng/g dw and 4 ng/g dw for 4,4’-DDE and 4,4’-DDT, respectively. Similar to the results obtained for water and air the lowest sediment concentrations were detected at Steinerne Renne. For this sampling location the highest concentration recorded within all OCPs was 0.6 ng 4,4’-DDT /g dw.

Since the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV, 1999) regulated that the amounts of benzo(a)pyrene, DDT and hexachlorobenzene in parks and leisure facility should not exceed 10 mg/kg, 200 mg/kg and 20 mg/kg, respectively, the highest values of 802 ng BaP/g dw, 12549 pg HCB/g dw and 12186 DDT pg/g dw, respectively did not exceed these levels.

* 1. **POP exchange (ratios) within environmental compartments in relation to contaminant physicochemical properties**

Based on the samples collected in Holtemme River the relationships between VO-matrices including water, sediment and air and log Kow and log Henry constant for PAHs, PCBs, and OCPs were investigated (Tables 11S and 12S). The ratios were calculated along different sampling periods and were dimensionless.

*Association between air and water*

Correlations of R2 0.77 and 0.84 were found between air/water ratios and log Henry constant related to PAHs and OCPs, respectively (Table 11S). The results suggested a tendency of positive relationship between the ratios and the investigated constants. Due to recorded large number of not detected PCB values in air samples the relationship with log Henry’s constant could not be studied.

*Comparing fugacities of air and water*

Figure 4 shows the relations of all pairwise existing data during all sampling period and for all chemicals at sampling station Holtemme/Nienhagen. The pairwise data for each chemical category of PAH, PCB and OCP regarding all sampling period is presented in Figure 4S-6S. This sampling spot was richest in pairwise data. It can be clearly seen that almost all data showed higher fugacities in water than in air, resulting in mass transport from water to air. For some quite volatile compounds such as hexachlorobutadien and pentachloroanisol the fugacities in air are slightly higher (upper part of the concentration range). Some few compounds in the middle range of concentration are PAH compounds which might have been locally released to airborne sources such as heating and traffic. However, in total the Holtemme River is the source of the air constituents at this particular sampling location.

Fig. 4

*Association between sediment and water*

A significant linear correlation (R2) of about mean 0.94, 0.92 and 0.83 was found between sediment/water ratios and log Kow for PAHs, PCBs and OCPs, respectively for the different sampling periods (Table 12S). These correlations regarding water-sediment exchange of POPs can be used to assess the equilibrium for individual compounds.

* 1. **POPs distribution within environmental compartments in relation to water flow rate and season**

The ratios of sediment/water and air/water were correlated to the flow rates (m3/s) during the investigated sampling periods in Holtemme River. The results suggested that these correlations have to be considered in relation to seasonality.

Profound correlations between sediment/water ratios and sampling flow rates was observed in the samples collected during the “summer” period of the year (Table 2S) in respect to PAH and PCBs (data not shown). It was found that the higher the ratio the lower the flow rate.

During the “summer” months, the PAH amounts as well as PCBs in air sample were mainly presented as zero or not detected (n.d.) values. However, poor correlations (R2) for the air/water ratios and flow rates in samples collected during “winter” period of the year were observed (data not shown). Due to small number of detectable OCP values in air samples the correlations for this group of substances were not studied.

* 1. **POP concentration levels in water and fat content in relation to water flow rate and season**

POP concentrations expressed in mass/L or mass/g fat for PAHs PCBs, and OCPs, respectively were directly correlated to the water flow rates (m3/s) of Holtheme River in relation to the winter and summer seasons. The results suggested that only samples collected during “summer” period of the year may show correlations between both parameters. It was found the higher the PAH and PCB i.e. water and fat content the higher the flow rate. Only four samples were selected for the “summer” months period a significant relationship for acenaphthene, fluorene, anthracene and PCB#28 was determined between the concentration levels (mass/g fat) and the flow rate (m3/s), respectively (Figure 5).

Figure 5.

Interestingly, an opposite relationship was found for the DDT-group suggesting that due to erosive remobilization from anaerobic zones, an increased amount with increasing of the flow rate was detected. 2,4’-DDD was the only congener within the DDT-group not showing a significant correlation (Figure 5).

* 1. **Relation between POP concentration levels in sediments and water flow rate and season**

No relationships were observed between PAH and PCB concentration levels (ng/g dw and pg/g dw) and water flow rates (m3/s), respectively. However, a considerable correlation was observed for the DDT-group as well as pentachlorobenzene and the flow rates during spring/summer months of the year (R2, in range of 0.63- 0.82) (data not shown).

1. **Conclusions**

In this study virtual organisms (VO) with fatty character have been employed to monitor air and water of small rivers and creek in a remote area in Germany. The generated data was expressed as mass concentrations also for triolein surrogating natural fat elaborating the potential accumulation of the POP from air and water into it. In addition, it was possible to report daily chemical freight for the sampling station with a gauge or nearby a gauge. A comparison of the freely dissolved water concentrations with the sediment exhibited close relationships pinpointing to a situation close to equilibrium for many of the chemicals investigated. According our calculation for water and fat and the chemical target analysis of sediments, the samples collected in Harz national park do not exceed the current regulatory limits. Comparison of PAH concentrations within investigated sampling locations suggests profound PAH levels in Nienhagen at Holtemme River for water, fat, air and sediment, respectively. Since several sampling campaigns were elaborated in this sampling area, the relationships between VO-matrices including water, sediment and air and log Kow and log Henry constant were investigated. Furthermore, a good relationship was illustrated for the sum of the daily mass transfer and the flow rate of the riverine system at location Steinerne Renne. The study manifests that POPs distribution within environmental compartments in relation to water flow rate have to be considered seasonally.

For the compartments air and water, we compared their fugacity, which clearly showed that for most of the chemicals the fugacity in water was higher. This indicates that the water is delivering mass to the air compartment. Only quite volatile compounds such as hexachlorobutadiene showed higher fugacity in air. VO are measuring the pure air and water concentrations; this is very useful since the pure concentrations are the proper basis for further calculations as well as (eco)toxicological exposure assessment (Bustos, 2016). That might be much more complicated and uncertain if grab sampling of either water or air is performed where sub-compartments such as aerosols or suspended matter etc. are biasing such assessments with quite high uncertainties. Another advantage of VO is that conservative worst case fat concentrations accumulating via air and water can be estimated, which are predictive and can be used for conservative limit investigations for food and nutrition.

However, it was also found that proper PRC design is mandatory to receive most reliable results of the corresponding compartments. The use of wide range of PRCs presented herein allows to improve the accuracy of the estimated water and air concentrations. Typical exposure times of about two months were perfect to integrate ambient concentrations so that even retrospective investigations are possible and no peak concentrations or hidden discharges such as the Cypermethrin case at Nienhagen station Holtemme river (Reiber et al. 2020) remained undisclosed.

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Figure 1. Sampling area in Harz National Park at rivers Wormsgraben as tributory to Holtemme (Drei Annen Hohne), Holtemme (Steinerne Renne and Nienhagen) and Selke (Meisdorf).

Source: Bundesanstalt für Gewässerkunde (2003): Hydrologischer Atlas von Deutschland (HAD), <https://geoportal.bafg.de/mapapps/resources/apps/HAD/index.html?lang=de>

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Figure 2. Average percentage PAHs homologue mass distribution (mass/g fat) and (mass/L) of water samples collected at different sampling locations, respectively.

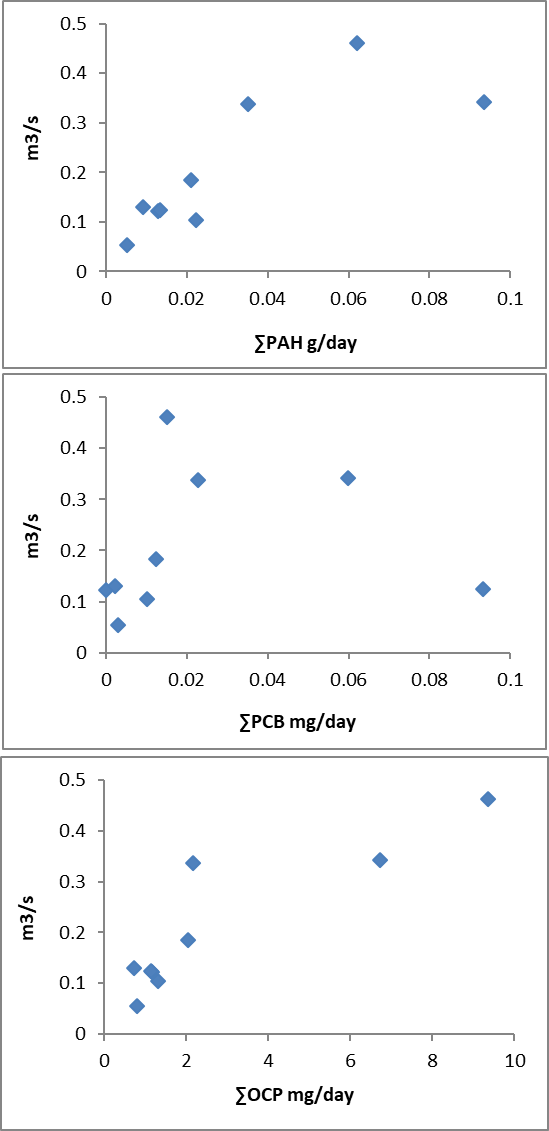


Figure 3. Relationship between the sum of the daily mass transfer (g/day and mg/day) and the mean flow rate (m3/s) of the riverine system at location Steinerne Renne.

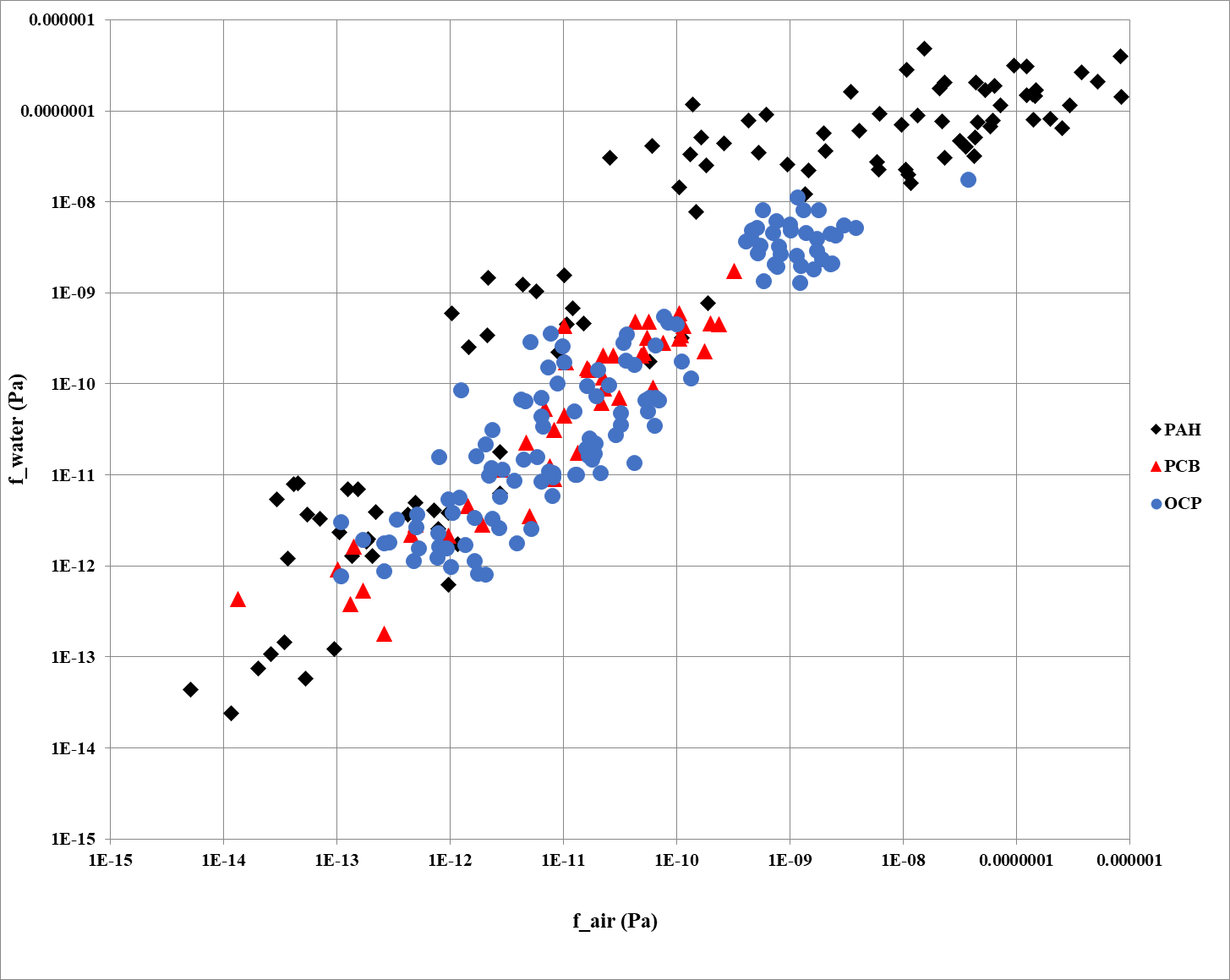


Figure 4. Comparison for fugacities of all compounds between air and water.

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Figure 5. Relationship between POPs concentrations (ng/L and pg/L) and water flow rate (m3/s) in water samples collected during warm season in Holtemme River.