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Deposition, persistence and turnover of pollutants: First results from the EU project AquaTerra for selected river basins and aquifers

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Abstract

Deposition, turnover and movement of persistent organic pollutants (POP) were investigated in the EU integrated project “AquaTerra”, which is among the first funded environmental projects within the 6th Framework Program by the European Commission. Project work integrates across various disciplines that range from biogeochemistry, environmental engineering, computer modelling and chemistry to socio-economic sciences. Field study areas are the river basins of the Ebro, the Meuse, the Elbe and the Danube as well as the 3-km^2 French catchment of the Brévilles Spring. Within the first 2 years of the project more than 1700 samples of atmospherically deposited particles, sediments, and water have been collected in the above-mentioned systems. Results show clear spatial patterns of deposition of polyaromatic hydrocarbons (PAHs) with the highest rates in the Meuse Basin. For local inputs, in the Brévilles sandy aquifer, the contamination of the groundwater by the pesticides atrazine (AT) and deethylatrazine did not decrease even 5 years after their agricultural inputs were stopped. On the other hand, herbicides such as mecroprop (MCPP), and PAHs, were at least partially degraded microbiologically in laboratory studies with soils and aquifer material from selected sites. For sediment transport of contaminants, new flood sampling techniques revealed highest deposition rates of β-hexachlorocyclohexane (β−HCH) in river sediments at hotspot areas on the Mulde River in the Bitterfeld region (Elbe Basin, Germany). These selected preliminary results of AquaTerra help to improve fundamental understanding of persistent organic pollutants (POP) in the environment.

Keywords: Persistent organic pollutants (POP); Atrazine (AT); Polyaromatic hydrocarbons (PAHs); Deposition; Microbial turnover; EU river basins

1. Introduction

To date, the behaviour of organic and inorganic pollutants in soils, sediments, ground- and surface water at catchment or regional scales is poorly understood.

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This lack of understanding results in part from a limited knowledge about loading, mobility and turnover of pollutants and is further complicated by the complexity and heterogeneity of the systems. This leads to uncertainties about fate and transport of pollutants in the environment. The EU 6th Framework Integrated Project “AquaTerra” now addresses these issues and aims to provide the foundations for an improved understanding of the behaviour of environmental pollutants. Here we present the first results of some selected case studies of the project.

The work in AquaTerra integrates across various disciplines that range from biogeochemistry, environmental engineering, computer modelling and chemistry to socio-economic sciences. Activities involve researchers, but also practitioners and end-users such as policymakers, river basin managers as well as regional and urban land planners. Field study areas are in the river basins of the Ebro, the Meuse, the Elbe and the Danube as well as the small 3-km^2 French agricultural catchment of the Brévilles Spring (Fig. 1). Within the first 2 years of the project, integrated work among the various partners has led to the collection of more than 1700 soil, sediment, water and biological samples. Apart from increasing availability of specialist results, project activities also included various meetings, the publishing of internal reports and national as well as peer-reviewed manuscripts (Barth and Grathwohl, 2005; Barth et al., 2006; Beinhorn et al., 2005; Bernhard et al., 2005; Bertagnoli et al., 2006; Bertoldi et al., 2006; Botter et al., 2005, 2006; Brouyère, 2006; Chen et al., 2005; Eljarrat and Barcelo, 2006; Eljarrat et al., 2005a,b, 2004; Hermand and Holland, 2005; Hermand et al., 2006; Kalbacher et al., 2005; Kolditz and Bauer, 2004; Kolditz et al., 2005; Lacorte et al., 2006; Lair et al., 2006; Meyer and Hermand, 2005; Meyer et al., 2006; Ratola et al., 2006; Rigon et al., 2006; Rinaldo et al., 2006a,b; Roulier et al., 2006; Seuntjens et al., 2004; Van Beusekom et al., 2006; Zanotti et al., 2004). Further information about the project is available on the AquaTerra Website (http://www.eu-aquaterra.de/).

Specific objectives of the work presented here were:

- To find out whether distinct deposition patterns of persistent organic pollutants exist across Europe.

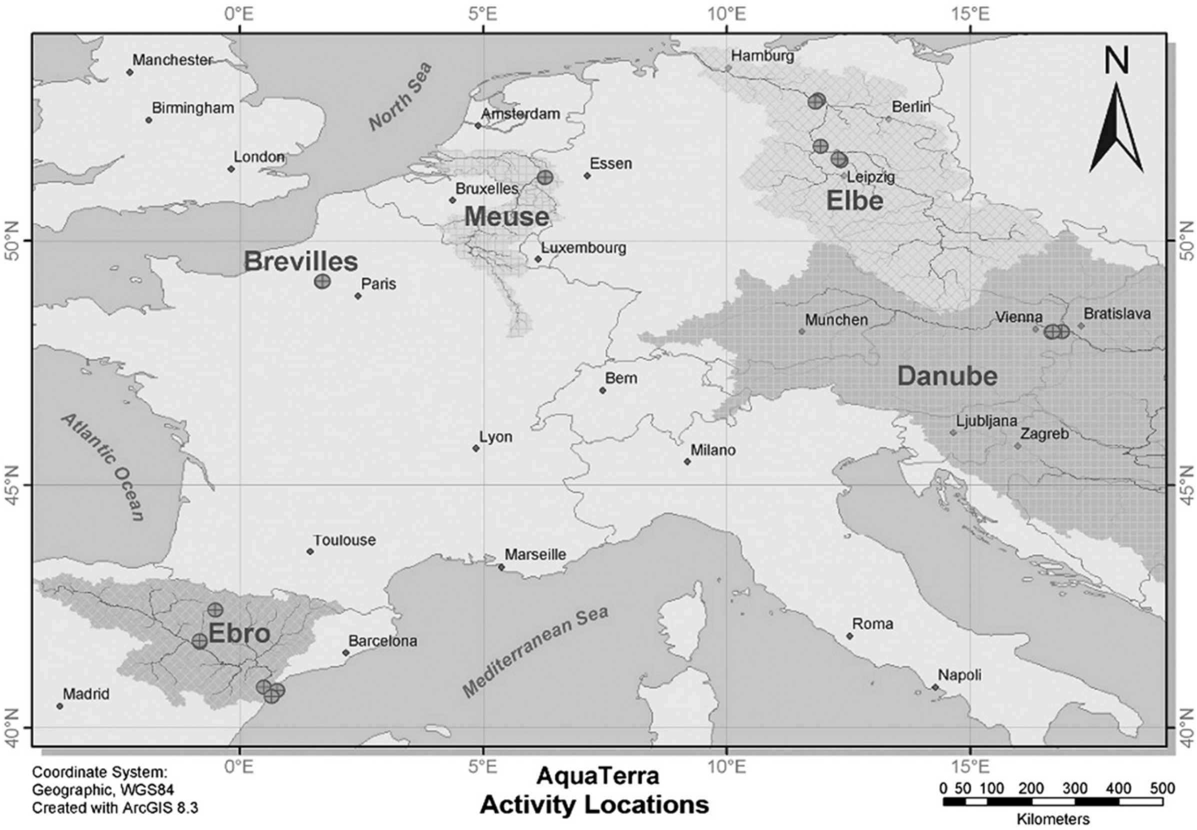

Fig. 1. Map of the areas investigated with round symbols marking the locations of the bulk deposition samplers.

This was determined with a specialised sampling technique using bulk deposition samplers and with focus on PAHs as an example compound class that is ubiquitously found in the environment.
- To determine the basin-wide mobility patterns of pollutants such as β-HCH, particularly caused by flooding, with a focus on the Elbe River by means of sediment investigations.
- To study the persistence of pesticides in a well instrumented pilot aquifer of the Brévilles spring. The small size (~3 km^2) of this catchment offers a unique opportunity to quantify inputs and outputs and to monitor Natural Attenuation of the system.
- To determine to what degree POP can be degraded in the environment. This was investigated in two separate laboratory studies with field samples from the Meuse and Brévilles using PAHs and MCPP respectively.

Despite the diversity of the regions studied and the different types of contaminants, all aspects presented here contribute to a better understanding of POP in the environment. Such fundamental understanding also helps to outline which challenges European research and policy is facing to ascertain good ecosystem functioning and to provide acceptable soil and water quality in the future.

2. Materials and methods

2.1. PAH deposition and analyses

Atmospheric dry and wet depositions of PAHs were determined using passive bulk samplers with a 250-mm diameter glass funnel connected to a glass cartridge (25 mm diameter) that was filled with 15 g of adsorber material (Amberlite® IRA-743). After about two-month sampling intervals, the cartridge was extracted and analysed for deposition rates in ng m^{-2} day^{-1} (Din19739—1,2, 2002; Martin and Grathwohl, 2002). PAHs were extracted with 200 mL of acetone and 10 mL of cyclohexane with 10 μL of 5 different deuterated PAHs (acenaphtene, crysene, naphthalene, phenantrene, perlyne) as internal standards. The extract was filled up to 2 L with de-ionised water and subsequent 48 h of storage at 20 °C caused the PAHs to migrate from acetone into the cyclohexane. The latter was then siphoned off and reduced to 1.5 mL by exposing it to a constant stream of N_2 gas. This extract was then further cleaned by channelling it through acetone-cleaned glass wool, 2 g of SiO_2 (Merck Silica Gel 60) and 2 g of Al_2O_3 (J. T. Baker). After a sequential elution with 15-mL isohexane, 5-mL isohexane/dichloromethane (9:1) and 20-mL isohexane/dichloromethane (4:1) the extract was rotary evaporated to a volume of 1.5 mL under a pressure of 350 mbar and at 35–40 °C. The cleaned extract was then analysed on a HP gas chromatograph (GC) (Model 5890) equipped with an autosampler and a mass selective (MS) detector (Model 5972) following the GC profile outlined by Gocht (2005). Repeat measurements in the laboratory revealed a precision of better than ±3% of each determined concentration. The precision of the sampler was determined in a field test with 8 replicates. The coefficient of variation was 5.1% for the PAH-sum and generally <10% for the single PAHs (Martin and Grathwohl, 2002). Because of occasional high naphthalene background contaminations found in field blanks, this compound was excluded and the results will be reported for the following compounds: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*) anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo (*e*)pyrene, benzo(*a*)pyrene, perylene, indeno(1,2,3-*cd*) pyrene, dibenz(*a*,*h*)anthracene, benzo(*ghi*)perylene. These correspond to the PAHs from the US-Environmental Protection Agency list.

2.2. Sediment sampling in the Elbe and HCH analyses

For Elbe flood investigations, sediments were collected on traps similar to artificial lawn that were placed in flood channels and on several terrace levels where they were inundated during floods. Collected sediments were removed from the traps, air-dried and sieved to a residual of 2 mm grain size. The top 20 cm of the floodplain soil from the same locations were also sampled in 5 cm steps and frozen at −20 °C until analysis. Before analysis, 0.75 to 20 g of dried sample were extracted for 18 h in a Soxhlet apparatus with 70 mL of a 2:1 hexane:acetone mixture. Extracts were then cleaned in an acid-base silica column and subsequently eluted with a 60-mL hexane:ethylacetate mixture (95:5). The eluates were then evaporated to about 0.1 mL and β-HCH was determined on a VARIAN 1200 Triple Quadrupole GC-MS using a 30-m VARIAN VF-5 ms capillary column at constant helium flow of 1.0 mL min^{-1}. D6-α-HCH served as the internal standard and D12-Perylene as the recovery standard. The analytical recovery calculated for each sample accounted for 96%±8% (standard error) with a range between 60 and 125%. Beyond that, analyses of reagent blanks and method blanks ensured quantifications free of contamination. The analytical precision of the GC-MS for repeated β-HCH measurements was <2.5%.

2.3. Pesticide inventory and analyses in the Brévilles catchment

Inputs of pesticides in the Brévilles catchment were evaluated through interviews with local farmers. This provided information about a minimal 10-year history of crop rotations and pesticide use as well as their active ingredients and doses. Monthly grab water samples were collected at the Brévilles spring in 1-L amber glass wide-mouth packers that meet quality standards for organic compounds. Samples were analyzed for atrazine, acetochlor, deethylatrazine, deisopropylatrazine, chlortoluron, isoproturon and two of its degradation products (monodemethylisoproturon, and didemethylisoproturon). After liquid–solid extraction, analyses were carried out by liquid chromatography/mass spectrometry with a LCQ DECA XP Plus instrument (Thermo Finnigan), except for acetochlor that was analysed by GC-MS (Varian GC 3800 with Saturn 2000 MS). The quantification limit for the eight products studied was 0.05 μg L^{-1}. Analytical recoveries were between 60 and 110% and corresponded to value ranges reported in other studies (Cai et al., 2004; Chee et al., 1996; Tomkins and Barnard, 2002). The expanded analytical uncertainty was determined between 10–20% and was in agreement with values reported for such compounds at concentrations of 0.1 μg L^{-1} (Chee et al., 1996; Quintana et al., 2001).

2.4. Sampling and experimental set-up of microcosms with MCPP

For microbiological pesticide degradation, drill cores were collected at the Brévilles site in plastic tubing. They were subsequently divided in suitable sections after visual inspection for contamination before being transported to the laboratory under cooled conditions by overnight carrier. Microcosms were set up to investigate the degradation of isoproturon, MCPP and acetochlor. Focus was put on MCPP degradation in the limestone and the aerobic sandy aquifer underlying the limestone. For the experiments, water from the Brévilles spring was first treated with activated carbon to remove pesticides and then sterile-filtered before being added to the sediment samples in the microcosms. With samples from the saturated zone, a total of 28 microcosms including 7 biologically inhibited controls (autoclaved 20 min., 1.5 bar, 120 °C, three times with one-day intervals) were set up to represent three different drilling locations and depths from 10.5 to 58.5 m below the surface (mbs). Aquifer samples were added to 118-mL glass serum bottles with 40 g sediment (wet weight) and 60-mL water from the Brévilles spring before being sealed with a 1 cm butyl stopper and crimp caps. 0.5 mL of ^{14}C-labelled pesticide stock solutions was added to achieve an initial concentration of ~ 1 μg L^{-1}. Subsamples of 2 mL were filtered and transferred to a double-vial system consisting of a 20-mL-polyethylene scintillation vial that contained another 6-mL-scintillation vial with 1-mL 0.5 M NaOH where $^{14}CO_2$ was trapped after acidification of the samples.

Samples from the unsaturated zone were collected from 4 drillings between 0.15 and 42.6 mbs and were set up similarly (70 microcosms including 20 controls), but without extra water. Incubation took place in the dark at 10 °C and ^{14}C-activity was quantified with a liquid scintillation analyser. The accuracy of the analyses was ±2.5% or better for the counting of the $^{14}CO_2$-concentration.

2.5. Experimental set-up microcosms with PAH

In order to investigate the aerobic and anaerobic biodegradation potential of aromatic compounds, incubations were set up with alluvial sediments from the unsaturated and saturated zone of a former cokery in the alluvial plain of the Meuse River (Luik, Belgium). 25 g of sediment was transferred into 50-mL-incubation bottles under an N_2 atmosphere. Then 15 mL of sterile filtered, anoxic groundwater amended with ^{13}C-labeled aromatic hydrocarbons (Cambridge Isotopes, Andover, MA) was added and bottles were closed using non-absorptive viton stoppers (Maagtechnic, Duebendorf, Switzerland). Substrate concentrations were similar to those of the source area with 44 mg L^{-1} benzene, 5 mg L^{-1} naphthalene and 1 mg L^{-1} acenaphthene. Microcosms were incubated in the dark at 16 °C without shaking. Samples from incubation experiments with ^{13}C-labelled compounds were analysed for the δ^{13}C signal of produced CO_2 using a gas chromatograph (Trace GC; Thermo Finnigan; Waltham; MA) connected via a combustion interface (Thermo Combustion III; Thermo Finnigan) to an isotope-ratio mass spectrometer (Delta plus XP; Thermo Finnigan). The helium carrier gas flow was 1.7 mL min^{-1} and CO_2 peaks were isolated with a 30-m PORAPLOT-Q column (inner diameter, 0.25 mm; film thickness, 10 μm; Varian, Palo Alto, CA) with the column temperature being held at 40 °C and CO_2 eluting after 240 s. The δ^{13}C values were calculated relative to external CO_2 reference gas using the relation

$$\delta^{13}\mathrm{C}[‰] = \left(\frac{{}^{13}\mathrm{C}_{\mathrm{sample}} / {}^{12}\mathrm{C}_{\mathit{sample}}}{{}^{13}\mathrm{C}_{\mathrm{standard}} / {}^{12}\mathrm{C}_{\mathrm{standard}}} - 1 \right) \times \ 1000 \ .$$

The uncertainty of the $^{13}C/^{12}C$ isotope analysis in CO_2 in long-term experiments with isotopically labelled substrates was $\Delta\delta^{13}C < 5$ [‰] and corresponded to maximum fluctuations in sterilized controls with ^{13}C-benzene within 135 days.

3. Results

In 2005, different deposition rates of the 17 most environmentally quantified PAH_{17} were found across Europe (Fig. 2) with the lowest ones in the Ebro basin ranging from 50 to 100 ng m^{-2} day^{-1}. Note that these do not include the winter season when usually higher deposition rates are found (Gocht and Grathwohl, 2004). For the Brévilles catchment we found an average deposition of 150–250 ng m^{-2} d^{-1}, for the Elbe basin 200–400 ng m^{-2} d^{-1}, and for the Danube and Meuse basins 300–600 ng m^{-2} d^{-1}. We are currently working on deciphering concentration distribution patterns of the 17 PAHs and their ratios at each location. These are then compared to similar analyses of concentration distributions in sediments, which are expected to provide inside into sources and turnover in the environment. This work will be published elsewhere.

In 2005, β-HCH, a waste product from the former local lindane (γ-HCH) production was found in amounts exceeding 10000 μg kg^{-1} in flood sediments and soils in the lower catchment area of the Mulde River, a main tributary of the river Elbe (Fig. 3). Peak β-HCH concentrations of 13,000 μg kg^{-1} were found at the site Spittelwasser, confirming the local above-limit values in fish of the Mulde. On the other hand, at the Czech site and upstream of the Spittelwasser inflow to the Mulde the contamination with β-HCH was below 0.3 and 10 μg kg^{-1} for collected sediments and soils, respectively. After the inflow of the Mulde into the Elbe, lower concentrations were found at the site Breitenhagen due to diluting effects of the upstream Elbe. Towards the site Schönberg, the concentrations of β-HCH decreased further, which is attributed to the diluting effect of the Saale Tributary that carries little β-HCH. Except for the source area of the Mulde River, the investigated sediments showed lower β-HCH values in the trapped sediments than in the investigated upper soil layers.

On the smaller scale Brévilles catchment, atrazine (AT) was detected in all of the groundwater and spring samples collected between June 2004 and April 2006 with concentrations varying between 0.12 and 0.22 μg L^{-1} (Fig. 4). These concentrations persisted despite the banning of the product since April 1999. Deethylatrazine (DEA), a major metabolite of AT, was also systematically detected in the spring, with concentrations between 0.55 and 1.05 μg L^{-1}. The total amount of AT and DEA that annually leaves the catchment ranged from 0.9 to 2.8% of the annually applied AT prior to 1999 (Morvan et al., 2006). Traces of deisopropylatrazine were occasionally observed, but other compounds such as acetochlor, isoproturon and its demethylated metabolites, and chlortoluron were not detected during the monitored period.

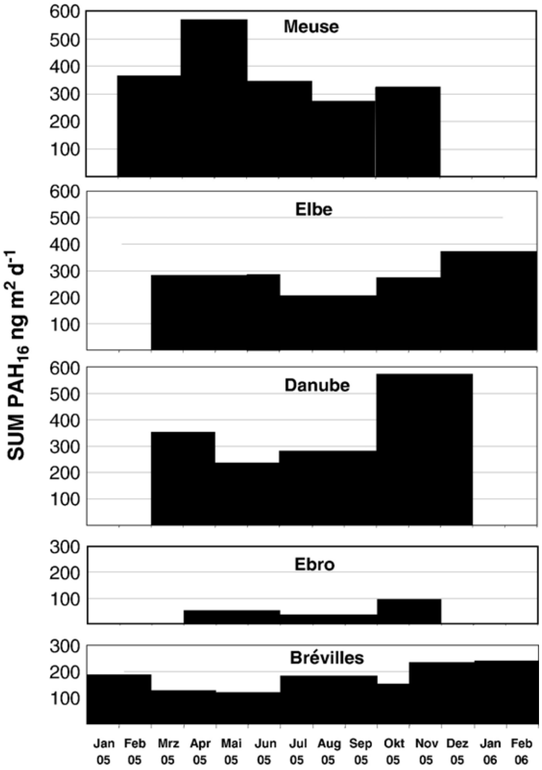

Fig. 2. Average PAH deposition rates measured in the five catchments. PAH16 consisting of the 16 PAHs: acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benz(*a*) anthracene, chrysene, benzo(*b*+*k*)fluoranthene, benzo(*e*)pyrene, benzo(*a*)pyrene, perylene, indeno(1,2,3-*cd*)pyrene, dibenz(*a*,*h*)anthracene, benzo(*ghi*)perylene.

On the other hand, selected herbicides such as MCPP could be biodegraded by bacteria present in soil and aquifer material from the Brévilles site. This process decreased in efficiency at greater depths. In the upper part (0.15–0.6 mbs) of the unsaturated zone a substantial degradation of 9–16 % was indicated by $^{14}CO_2$-production already 14 days after initiation of the experiments. After 91 days 25–34% of the added ^{14}C-MCPP was mineralized to $^{14}CO_2$ (Fig. 5). After 78 days, degradation was also observed in greater depths around

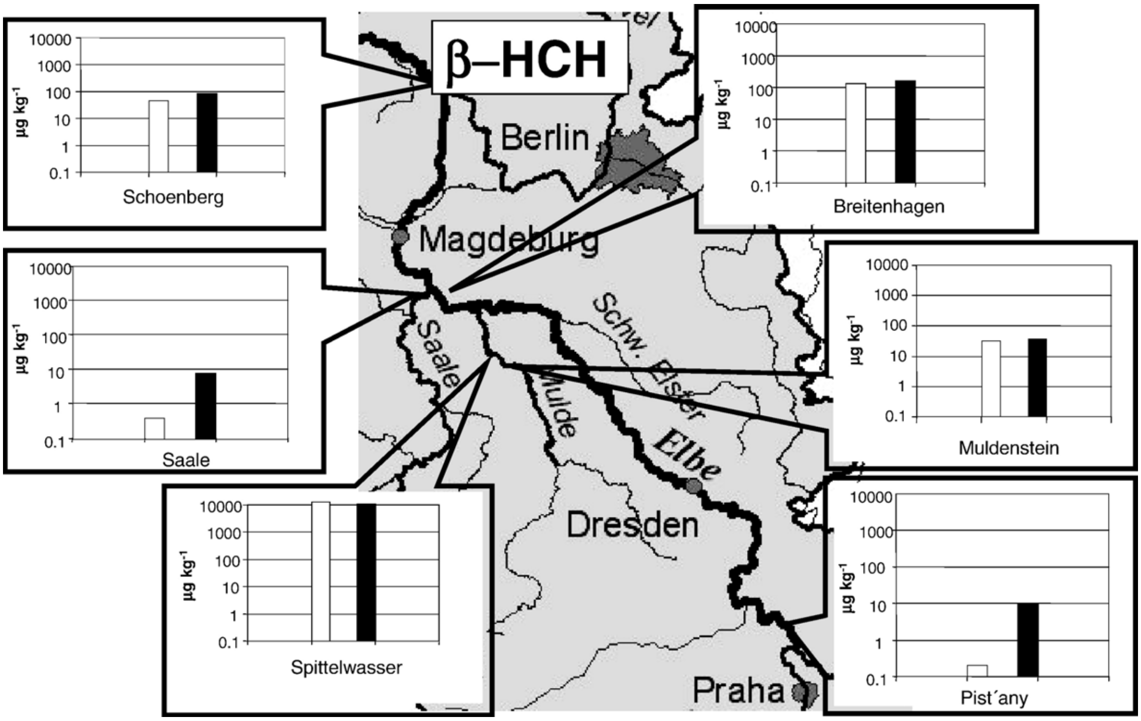

Fig. 3. Distributions of β-hexachloroyclohexane (β-HCH) in the Elbe Basin. The black columns in the diagram represent results from the upper 5 cm of floodplain soil and the white columns data from the sediment traps.

19.5 mbs where 11–16% of the initially added ^{14}C-MCPP was recovered as $^{14}CO_2$ (data not shown here). The highest extent of mineralization was observed in one selected drill hole where 22% of the compound was degraded at 4.5 mbs, 12% at 4.8 mbs and 10% at 5.8 mbs, but in another drill hole nearby also 4% was

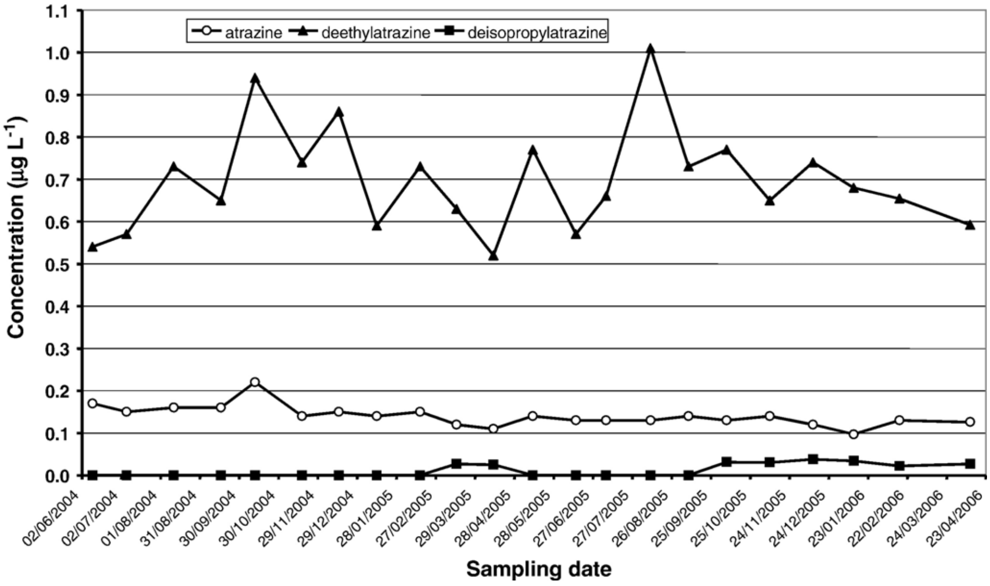

Fig. 4. Time series of atrazine, deethylatrazine and deisopropylatrazine concentrations in the Brévilles spring (June 2004–April 2006).

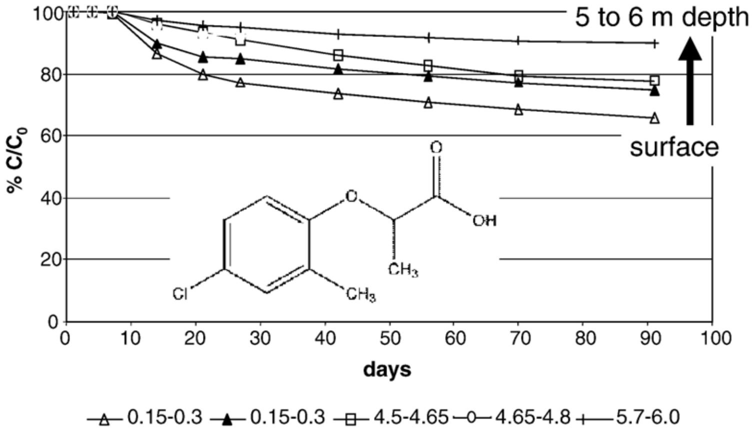

Fig. 5. Mecroprop (MCPP) degradation as a function of soil depth. The different symbols represent samples taken in meters below ground.

degraded at 6.8 mbs. Even in samples from greater sampling depths (58 mbs) a small, but noticeable $^{14}CO_2$-production was observed after more than 200 days of incubation.

Applying a similar concept of labelled stable isotope compounds biodegradation of aromatic compounds on the Flémalle site, enrichment of ^{13}C-CO_2 in the gas phase occurred in aerobic microcosms amended with ^{13}C-benzene and ^{13}C-naphthalene within several days. Aerobic biodegradation of ^{13}C-acenaphthene by the bacterial community started after a lag-phase of 7 to 10 days and was also found to be considerably slower than degradation of benzene or naphthalene. In absence of O_2, biodegradation of benzene and naphthalene started after a lag phase of several days. In contrast, under anoxic conditions degradation of acenaphthene was almost negligible over a period of >150 days of incubation (Fig. 6). In a related microcosm experiment, degradation trends were comparable for three different depth layers of the saturated zone. Moreover, the intrinsic biodegradation potential did not strictly decrease with sediment depth, but rather seemed to be related to sediment types. In microcosms containing loose sand-gravel sediments from 9 and 12 m depth, initiation of degradation of ^{13}C-benzene and ^{13}C-naphthalene occurred significantly faster compared to degradation in less permeable loamy sediments from 7 m depth (Fig. 7).

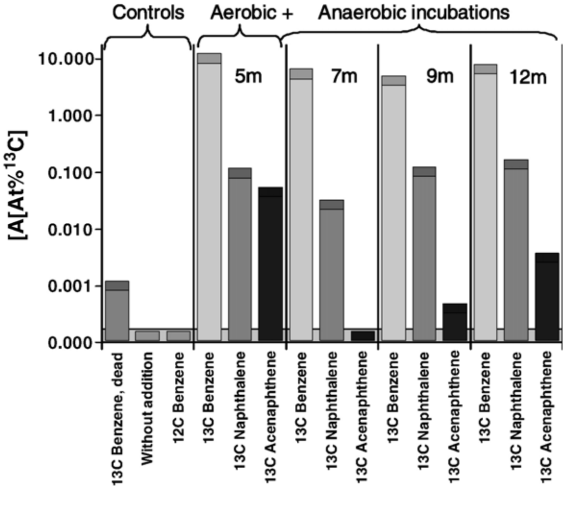

Fig. 6. Maximum increase in ^{13}C-CO_2 in the headspace of microcosms within 244 days of incubation (acenaphthene within 158 days) shown in atom percent defined as At.%^{13}C $= \left[\frac{^{13}C}{^{12}C+^{13}C}\right] \times 100$. Controls were either autoclaved, without substrate addition or with non-labelled benzene.

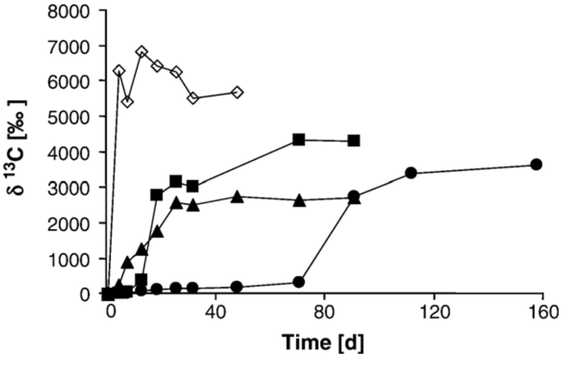

Fig. 7. Increase in ^{13}C-CO_2 in the headspace of microcosms during the degradation of naphthalene with sediment sampled from depths of 5 m (◇), 7 m (●), 9 m (▲), and 12 m (■).

4. Discussion

Atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) is a good measure to compare the input of persistent organic pollutants across the various basins. Nevertheless, it has to be kept in mind that sampling occurs predominantly at selected rural locations of each catchment. Therefore measured deposition rates cannot necessarily be regarded as representative for a given entire catchment. This is only the case for the 3-km^2 Brévilles catchment where 3 deposition samplers were installed. Other results from Germany obtained with the same technique are comparable with the deposition rates of this study with 450–1600 ng m^{-2} d^{-1} for the city of Kehl and 150–600 ng m^{-2} d^{-1} for the rural Schauinsland mountain (PAH$_{12}$, phenanthrene-benzo(*ghi*) perylene). Gocht (2005) also investigated rural areas and found an annual average of 160 ng m^{-2} d^{-1} of benz(*a*)anthracene- and benzo(*ghi*)perylene for a sub-catchment in the Schönbuch forest and 270 ng·m^{-2}·d^{-1} for the Seebach catchment in the Black Forest.

In terms of β-HCH deposition from a hotspot production area in the Mulde Catchment, the input via new flood sediments into the floodplains was lower than the already present contamination of the floodplains themselves. Nevertheless, we found a diluting effect through the sediment transport in recent flood sediments. This happened when lower concentrated suspended sediments of the upstream Elbe or the Saale tributary mixed with sediments transported by the Mulde. This shows that downstream contaminant transport of pollutants particularly when associated with particles and floods are complex. With the dilution effects and stepwise propagation by floods, our results also indicate that downstream propagation of pollutants can take years to decades.

For pollutants such as pesticides in a well-delineated catchment, the persistence of AT and DEA concentrations in the groundwater even 5 years after their last application may have resulted from a combination of factors including storage and/or a very slow overall transport through the catchment. The former possibility is at least partly true as the compounds in question were found to adsorb onto the soil (Dagnac et al., 2005) and significant sorption capacity of some vadose zone solids could be demonstrated (Clausen et al., 2004). On the other hand, the transit time of the compounds through the several meters thick vadose zone may exceed the time elapsed since the application of AT was halted. Each of these hypotheses is equally likely and all of the mechanisms considered have an influence in generating the small but consistent pesticide signals at the spring. Furthermore, the degradation of AT and DEA in the deeper vadose zone and in the saturated zone is probably small. This was examined by laboratory incubations with samples from the Brévilles limestone that underlies the first meter of soil, and from sand, which revealed no degradation of AT nor DEA during a 2-year incubation period (Albrechtsen et al., 2003). In any case, the degradation potential for selected herbicides such as MCPP could be clearly demonstrated in laboratory conditions with material from the Brévilles catchment. We also found a clear tendency of declining degradation with depth of this relatively easy degradable pesticide. The fact that biodegradation occurs for such selected pesticides in conditions reflecting the saturated zone of a groundwater body suggests that Natural Attenuation in the saturated zone may have to be considered in mass balance considerations.

For PAH hotspots such as the former cokery site of Flémalle, a potential for biological turnover of aromatic hydrocarbons was distributed over the entire site and equally detected in sediments sampled up-gradient of the contamination sources. Therefore, the presence and activity of PAH-degrading bacteria was not only restricted to contaminated sediments. However, as the site is located in a highly industrialized region, it cannot be ruled out that sediments at the reference point were affected by contaminants from other sources in the past. The fact that degraders of mono- and poly-aromatic compounds are widespread in alluvial sediments and moreover are active under anoxic conditions suggested that biodegradation of low molecular weight mono- and poly-aromatic compounds should be possible elsewhere for instance at sites of high atmospheric deposition. The Flémalle study also confirms that mono- and di-aromatic compounds are more easily degradable than higher molecular weight PAHs. One reason for this trend might be the limited water solubility of larger molecules and their resulting decreased availability for bacterial biodegradation. The larger molecules are also more stable and more difficult for bacteria to transport into their cells and are thus less susceptible to microbial degradation. The fact that loamy sediments are less permeated by groundwater may limit biodegradation by insufficient nutrient supply, whereas in more permeable sediments higher degradation rates of contaminants are more likely to occur.

5. Conclusions

The sources of contamination of the presented pollutants ranged from atmospheric deposition, via spreading from hotspots through flooding, agricultural and industrial input. These forms of pollutant input and subsequent behaviour are often typical for a specific compartment and area. For instance mobilisation of contaminants in floodplains in the Elbe River is difficult to compare to turnover of pollutants in soils of the contaminated Flémalle site. Other specific soil, sediment surface- and groundwater investigations were carried out in the Ebro and Danube area but will be presented elsewhere.

First results showed strong variations in atmospheric deposition of PAHs within and between the basins studied and results were presented on the Ebro, Danube, Elbe, Meuse and Brévilles areas. These differences are probably caused by local influences such as adjacent industrial areas. To which extent these patterns are influenced by climatic factors such as wind direction and varying influences of wet and dry deposition in the different climatic zones remains to be explored with further consideration of seasonal variations and concentration analyses of the individual PAH. Similar deposition patterns for pesticides and HCH may also exist, however at much smaller concentrations as these compounds rather seem to have point sources of input and are less ubiquitously distributed in the environment.

Regardless of the source, it is also important to investigate how the pollutants behave in the environment with respect to their spreading, residence times, sorption and degradation. For flood plains of the Elbe River we observed dilution effects during sedimentary spreading from HCH hotspots in the Mulde Tributary. While sorption and degradation have not yet been investigated for this compound group, its continuous downriver spreading is less severe than the contamination of the already present soil. Nevertheless, the impact of HCH on the biological communities in aquatic environments and in the flood plains as well as its incorporation into the food chain need further research that is partially being addressed with biomonitorig techniques in AquaTerra.

Specific PAH degradation experiments from the Flémalle site outlined similar degradation potentials in unpolluted areas since soils upstream of the pollution hot spot seemed to perform equally well in experiments. However, degradation in the field may operate differently than under controlled laboratory conditions, thus setting focus for future research. This includes investigation of effects such as the dependency on concentrations or influences by local climate that still need further investigation.

While biodegradation of key pesticides such as atrazine was not measurable in the Brévilles Catchment with material from deeper layers than the root zones, we could prove degradation of proxy compounds such as MCPP down to 58 m below the soil surface. However, this degradation occurred with decreasing efficiency in deeper layers. Even though degradation rates are very low in greater depths, they should be considered in risk assessment and in modelling the fate of pesticides, particularly when considering long hydraulic residence times of small aquifers such as the Brévilles. Such residence times would presumably be much longer in larger catchments and river basins and thus enable even slow rates of degradation. Further investigations of small-scale concentration variations may also reveal more active degrading layers on the cm-scale.

Overall, despite the variability of the compounds and compartments studied (atmosphere, soil, sediments, water) the above work outlines the challenges and benefits to consider catchments as a whole. It is nevertheless important to note that the different compartments studied often have specific environmental concerns in specific regions. For instance soil and groundwater pollution through pesticides seems to be a pronounced problem in the Brévilles where this concern is being addressed in a well-instrumented catchment that allows detailed monitoring. Detailed results and suggested solutions from this research will also be transferable to other areas of similar concern. As for diffuse pollution such as deposition of PAHs perhaps the best comparisons can be drawn with the passive sampling techniques presented in this manuscript.

Nevertheless, ongoing and future work also has to include further input–output mass balances on larger scales that also consider pollutant storage and turnover. Current and future work of AquaTerra will cover aspects of ground- and surface water interaction as well as sediment transport in the Elbe, Meuse, Danube and Ebro Basins as well as the catchment of the Brévilles spring. It will also address the mobility and turnover of organic pollutants such as pesticides and polyaromatic hydrocarbons and includes various aspects of metal behaviour in soils, sediments and floodplains. Further work will also focus on field and laboratory techniques such as integral pumping tests and groundwater dating while other workers introduce new aspects of biomonitoring by field-based techniques as well as modelling. Further modelling studies of surface- and groundwater hydrology in the context of climate change are also under way, while overall considerations on challenges to link science with policy are being discussed by socioeconomic specialists in AquaTerra. Most of this work will be represented in the peer-reviewed literature such as for instance an almost complete special issue in the journal Environmental Pollution.

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