



Research article

Occurrence and levels of micropollutants across environmental and engineered compartments in Austria



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ABSTRACT

Occurrence and concentration of a broad spectrum of micropollutants are investigated in Austrian river catchments, namely polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), organotin compounds, perfluoroalkyl acids (PFAAs) and metals. The parallel analysis across multiple environmental and engineered compartments sheds light on the ratio of dissolved and particulate transport and on differences in concentration levels between point and diffuse emission pathways. It is found that some PAHs and organotins are present in rivers, groundwater and bulk deposition at higher concentrations than in municipal wastewater effluents. Among PFAAs and metals, highest concentrations were recorded either in atmospheric deposition or in discharges from wastewater treatment plants. The relevance of the analysis across compartments is best shown by the case of perfluorooctanesulfonic acid (PFOS). Despite municipal wastewater effluents being the emission pathway with highest concentrations, this study reveals that not only rivers, but also atmospheric deposition and groundwater sometimes exceed the environmental quality standard for surface waters. Moreover, this work reveals partially counterintuitive patterns. In rivers with treated wastewater discharges, increasing levels of dissolved compounds were measured at rising flow conditions, whereas the opposite would be expected owing to the dilution effect. This might derive from the mobilisation from soil or suspended particulate matter or rather find its explanation in high concentrations in atmospheric deposition. These hypotheses require however being tested through targeted studies. Additional future research includes the analysis of how regional or catchment specific characteristics might alter the relative importance of different emission pathways, and the modelling of emission and river loads to assess their relative contribution to river pollution.

1. Introduction

Several trace metals and organic micropollutants are either still directly emitted or are transported to and between water bodies due to contamination legacy. Many of them are persistent, ubiquitous and bioaccumulative, and their presence in water resources may pose a risk to the health of humans and wildlife. The European Union has carried out a prioritisation of the trace contaminants which are considered most critical for the water resources on its territory. For the selected compounds, Environmental Quality Standards (EQS) have been established, and member countries are required to reduce and ultimately eliminate emissions (EU, 2008, 2013). The twofold objective of reducing/eliminating emissions and of demonstrating compliance with EQS

necessarily requires a detailed knowledge and understanding of the status quo. However, a good comprehension of the current situation is often still challenging. One first obstacle is the technical limitation of the analytical procedures employed in routine monitoring schemes, which is mostly not adequate to robustly compare measurements with EQS nor to develop or validate emission modelling, due to the high limits of quantification and detection that frequently fail to deliver quantitative results (Brack et al., 2017). A second barrier is the poor-ness and sometimes the complete lack of information on occurrence and concentration levels of trace pollutants in different environmental and engineered compartments, which contribute directly or indirectly to water contamination. Published research in this field typically focuses on one or few selected media. Integrative assessments aiming at

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Table 1
Main characteristics of the nine case-study catchments.

| | Pram | HOAL | Öztaler Ache | Reichramingbach | Mattig | Birkengraben | Dornbirnerach | Raba | Wulka |
|---|------|--------|-----------------|-----------------|--------|--------------|---------------|------|-------|
| Total area [km ²] | 83 | 0.66 | 892 | 171 | 450 | 4.3 | 196 | 1009 | 404 |
| Arable land [%] | 45 | 83 | 0 | 0 | 14 | 7 | 5 | 25 | 51 |
| Grassland [%] | 27 | 7 | 52 | 5 | 31 | 75 | 20 | 17 | 2 |
| Forest [%] | 23 | 7 | 15 | 89 | 48 | 1 | 51 | 52 | 40 |
| Bare areas [%] | 0 | 0 | 32 ^a | 2 | 0 | 3 | 1 | 0 | 0 |
| Urban areas [%] | 3 | 3 | 0 | 0 | 4 | 12 | 19 | 3 | 5 |
| Others [%] | 2 | 0 | 1 | 4 | 3 | 2 | 4 | 3 | 2 |
| Avg. ratio WW to total flow [%] | 2 | 0 | <1 | 0 | 3 | 0 | 9 | 3 | 36 |
| Mean flow [m ³ s ⁻¹] | 1.2 | 0.0041 | 31 | 6.3 | 5.7 | 0.28 | 6.9 | 9.9 | 1.6 |
| Mean precipitation [mm yr ⁻¹] | 1004 | 932 | 1112 | 1680 | 1252 | 1555 | 1700 | 833 | 695 |

^a Out of the total bare areas, 34% are occupied by glacier, whereas the rest consist of alpine bare rock.

investigating the relevance of different emission pathways have thus to rely on fragmented data, with often considerable spatial and temporal discrepancies. Given the above, this work aims to identify the occurrence and to quantify the concentration level of micropollutants in Austrian river catchments. The major novelty is the simultaneous investigation of a broad spectrum of compounds in several environmental and engineered compartments. The study areas are distributed throughout the country, so to cover different geographical, climatic and land-use related characteristics. Multiple compartments are examined simultaneously with the goal of shedding light on the potential importance of different transport and emission pathways. This study should therefore be relevant both for institutional bodies which need to prioritize their monitoring and management strategies, and for international scientists interested in better understanding the diffusion and the transport of micropollutants into water bodies. To investigate the level of contamination in water bodies, groundwater and both dissolved phase and suspended particulate matter (SPM) in river water are examined. SPM is chosen over sediments because it better reflects the current contamination status, and also in virtue of its higher percentage of fine-grained fraction, in which particulate-bound contaminants mainly accumulate (Schubert et al., 2012). To gain insight into point and diffuse emission pathways, effluents of municipal and industrial wastewater treatment plants (WWTPs), soils and bulk atmospheric deposition are investigated. As far as the analytical spectrum is concerned, the scope of the study includes the following contaminants:

- metals: mercury (Hg), cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu), and zinc (Zn);
- organotin compounds: monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), tetrabutyltin (TeBT), diphenyltin (DPhT), and triphenyltin (TPhT);
- polycyclic aromatic hydrocarbons (U.S. EPA PAH₁₆): naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), benzo(g,h,i)perylene (BPE), dibenz(a,h)anthracene (DHA), and indeno(123-cd)pyrene (IPY);
- polybrominated diphenyl ethers (pentaBDE congeners): BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154;
- perfluoroalkyl acids (PFAAs, according to the definition of Buck et al. (2011): perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA).

These specific groups were selected on the one hand because they are ubiquitous and are thus optimal to investigate occurrence and relevance of different emission pathways, and on the other hand because based on previous monitoring outcomes they are considered particularly relevant for the compliance of Austrian water bodies with the objectives of the European Water Framework Directive. As the main novelty and focus of the study consist of the parallel examination of

several substances in many different compartments, it is based on a sampling design which enables examining time-integrated occurrence and concentration ranges.

2. Materials and methods

2.1. Monitoring network and sampling design

2.1.1. Specific case-study catchments

Nine specific river catchments were selected with the twofold goal to examine contamination levels across a heterogeneous territory and to investigate the existence of relationships between different emission pathways and between concentration levels at different flow conditions. The selection includes two catchments dominated by arable land (Pram and HOAL), two alpine forest catchments (Öztaler Ache and Reichramingbach), and two lowland catchments with large areas dedicated to grassland (Mattig and Birkengraben). In all six, the average contribution of wastewater effluents to the total river discharge at mean flow condition is minimal, ranging from null to 3%. This characteristic enables the focus on diffuse emissions pathways. In addition, three catchments with more heterogeneous land use, presence of industry and relevant contribution of wastewater discharge to total river flow were selected (Dornbirnerach, Raba and Wulka). The nine case-studies are also representative of the geographical and climatic diversity within the Austrian territory. They are distributed from east to west and they cover a wide range of average precipitation, from 695 mm yr⁻¹ to 1700 mm yr⁻¹. Catchment size is also diverse. It ranges from 83 to 1009 km². An exception is constituted by a headwater agricultural catchment of 66 ha located approximately 100 km west from Vienna. This case-study was selected in virtue of its role as Hydrological Open Air Laboratory (HOAL), jointly operated by the TU Wien and the Federal Agency for Water Management (BAW) (Blöschl et al., 2016). Therefore, despite its much smaller size, it offered advantages with respect to logistics and data availability. The main characteristics of these case-studies are reported in Table 1, whereas their location and catchment borders are shown in Fig. 1.

In these catchments, stream water, suspended particulate matter, soil and bulk deposition were analysed to investigate time-integrated concentration levels of the whole spectrum of substances addressed in this study.

2.1.1.1. River water. The sampling scheme for stream water was designed with the goal to characterise average concentrations at baseflow and high flow conditions. Sampling took place from July 2016 to August 2017 and owing to logistical constraints it was organised differently in the nine catchments. In the two catchments of Birkengraben and Dornbirnerach a 11 grab sample was collected weekly, whilst 51 grab samples were taken monthly in the other catchments. Further, a target sampling during high flow conditions was performed, either manually or via autosamplers. High flow conditions in this study were defined as storm events in which a

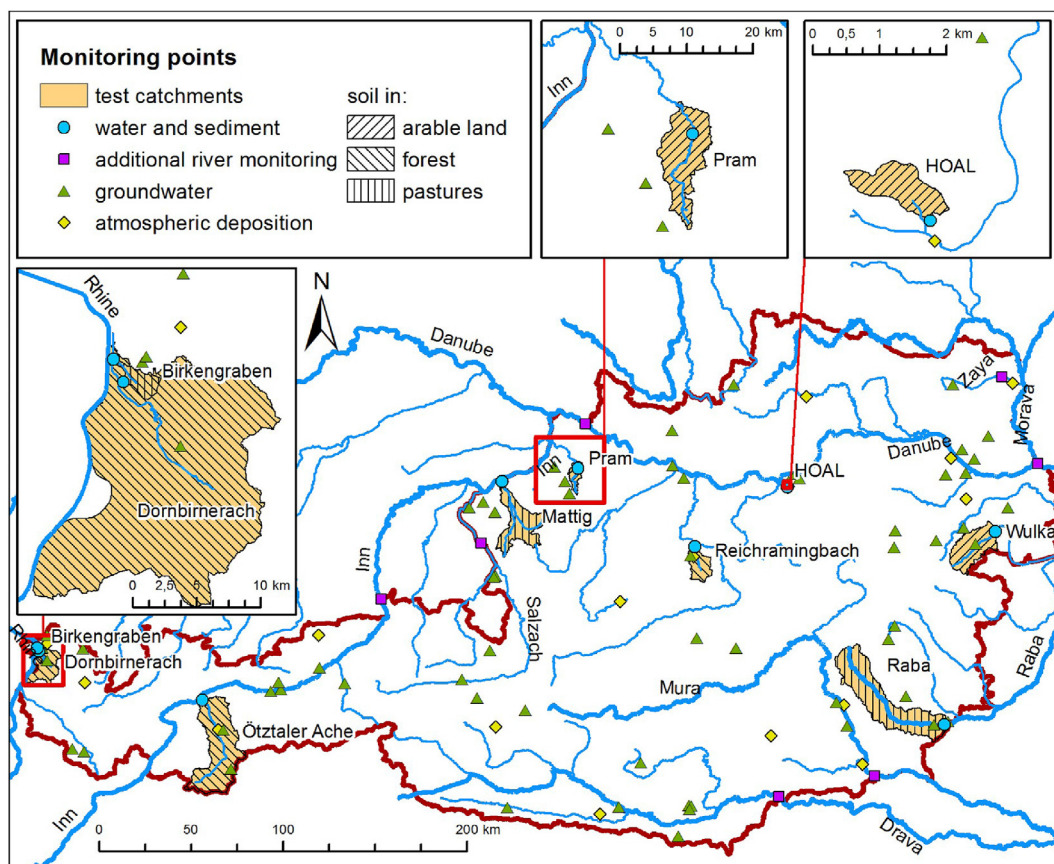


Fig. 1. Map with sampling locations and borders of specific case-study catchments. Note: location of municipal and industrial WWTPs is not displayed owing to anonymity agreements.

significant and durable raise in both discharge and turbidity was recorded. At storm events, a volume of 10 l was taken. After filtration, all samples were frozen for their preservation. Immediately prior to their analysis, samples were thawed and combined in order to obtain for each catchment two composite samples representative of baseflow and two composite samples representative of high flow conditions. In addition, 11 water samples were regularly taken in parallel to the large volume samples and were immediately analysed to measure standard chemical parameters, such as total suspended solids, total and dissolved organic matter as well as total and dissolved nutrients.

2.1.1.2. Suspended particulate matter. The analysis of the micropollutants object of this study in the solid matrix requires the availability of a minimum amount of material of at least 150 g dry weight (dw). To achieve this, suspended load samplers specifically designed to trap and collect SPM were installed at each river. These samplers, developed and tested by the Environment Agency Austria in a previous project (Gans et al., 2012), are based on the principle of sedimentation. An inlet device fixed within the river was connected with the sampler by a Teflon-free tubing of several meters length. Where a sufficient natural slope gradient was not available, a pump was installed to ensure a continuous water supply. The sampler is designed in a way that only a small portion ($0.001\text{--}0.002\text{ l s}^{-1}$) of the river water can flow down, through a central pipe by gravitational force, to the bottom of a 25 l round HDPE container. Due to the large diameter of the container, the water rises very slowly (1–3 h) and is released through a small overflow-pipe allowing a nearly complete settling and/or flocculation (80–90%) of the suspended load in the container. For one year (from July 2016 to August 2017), the containers were brought to the laboratory on a monthly basis. There, the suspended load was

recovered by settling in large plexiglass cylinders and was subsequently lyophilised. The lyophilised material was mixed according to the river discharge values recorded during the corresponding sampling periods, in order to obtain for each catchment two composite samples of SPM transported during high flow and one composite sample representative of baseflow conditions.

2.1.1.3. Soil. The sampling of soil was designed with the goal to characterise specific land uses. Background forest soil was therefore sampled in the three alpine catchments of Dornbirnerach, Ötztaler Ache and Reichramingbach. Soil samples of grassland were taken instead in the catchments of the Birkengraben, Mattig and Raba. Arable soils were sampled in the HOAL and in the catchments of Pram and Wulka. In forest soils, samples were taken by means of a stainless steel frame (25 cm × 25 cm) at a depth of 0–5 cm, after previous removal of the litter layer. Grassland soils were collected through a Pürckhauer ground auger and an Edelman auger at a depth of 0–10 cm after removal of the grass layer. Arable soils were collected through the same augers, but at a depth of 0–30 cm. The sampling was performed in each catchment at 30 spots distributed from upstream to downstream to cover geographical and geological heterogeneity. Two such campaigns were performed in early winter 2016 and late spring/summer 2017. During the first campaign, the coordinates of the sampled spots were recorded through GPS, in order to enable the accurate repetition of the sampling in the second campaign. The samples were stored and bulked on site into 21 REX glass jars, immediately transported to the laboratory and there they were merged and homogenised to obtain composite samples of approximately 2 kg (Fresh Matter) for each catchment.

2.1.1.4. Bulk atmospheric deposition. The goal for the analysis of bulk deposition was to obtain composite yearly cumulated samples. This was

achieved with a diversified approach. In the HOAL, a stainless steel heated sampling device was installed and, from July 2016 to July 2017, it was emptied within maximum 48 h after each rainfall event. Cumulated samples were immediately frozen and stored in HDPE canisters. To investigate the deposition in the other case-study catchments and to extend the study to a vaster area, the project relied on 13 existing monitoring stations. Out of them, one station is operated by the Central Institution for Meteorology and Geodynamics (ZAMG, 2018) and 12 stations are operated by Environment Agency Austria, 11 of which are included within the ANIP network (Umweltbundesamt, 2018b). For all these stations, a fraction of the routinely collected samples was made available for this study and was stored from July 2016 to July 2017 at -20° in HDPE canisters, to generate a composite yearly sample. In addition, in the same period of time and following the same procedure, bulk deposition was collected through funnels in HDPE canisters in three cities (Vienna, Graz and Bregenz).

2.1.2. Complementary monitoring

In parallel to the investigation in the nine case-study catchments, additional specific campaigns were conducted with the twofold goal to extend the study to other natural and engineered compartments and to enhance the spatial resolution of the analysis. Fig. 1 depicts also the sampling points of these additional campaigns.

2.1.2.1. River water. The focus of this complementary monitoring campaign, conducted from October 2016 to August 2017, lied on large rivers, namely Danube, Drava, Mura, Inn, and Salzach. Additionally, the river Zaya was included, owing to its vulnerability to contamination, since it drains a relatively dry basin and it receives considerable discharges from WWTPs. Grab samples were collected on a bi-monthly basis and were immediately analysed to measure PFOS and PFOA. The rest was frozen and at the end of the campaign was combined to obtain a yearly composite sample for each river, where PBDEs, organotin compounds, Hg and Cd were investigated.

2.1.2.2. Groundwater. A representative sample of 64 groundwater monitoring sites included in the national water quality monitoring network were sampled in the third quarter of 2016 and second quarter of 2017. These monitoring sites represent different land uses (forest/natural vegetation, agriculture, urban/commercial/industrial) and diverse climatic and geological conditions in Austria. All compounds reported in Table 2 were analysed, except for Cu and Zn. For these two metals, unlike for all other contaminants examined here, more than half of the data provided by official routine monitoring is above the LOD and enables therefore a proper evaluation of concentration levels, without the need of an additional targeted campaign. For sake of completeness, this study includes also the evaluation of this national data, namely Cu and Zn measurements conducted in all available groundwater sampling sites between the second half of the year 2016 and the first half of 2017 (Umweltbundesamt, 2018a).

2.1.2.3. Municipal wastewater effluents. Eight municipal WWTPs were investigated. All plants share major characteristics typical of Austrian municipal wastewater treatment with state-of-the-art technology. Specifically, they consist of primary sedimentation, single-stage or two-stage activated sludge (average sludge retention time: 14–20 days), secondary clarification, sludge pre-thickening, mesophilic sludge digestion, sludge post-thickening and dewatering. Further, they all perform enhanced nitrogen and phosphorus removal, but implement no advanced removal of organic micropollutants. Nevertheless, they cover a broad spectrum of diverse installations. The first difference is the wastewater load, with two plants included in the range of 20,000–50,000 population equivalent (PE_{COD120}), three plants within the interval 50,000–150,000 PE_{COD120} , and three plants larger than 150,000 PE_{COD120} . Further, the ratio of combined sewer to

the total sewer system ranges from 70% to 95% and they treat different proportions of industrial wastewater stemming from a variety of sectors. From each plant, effluents were sampled at seven consecutive days four times. In the resulting flow-proportional composite samples, six heavy metals (Hg, Cd, Pb, Cu, Ni, Zn), PAH₁₆, penta-BDEs, PFOS, PFOA, DBT and TBT compounds were analysed.

2.1.2.4. Industrial wastewater effluents. The focus of this specific monitoring campaign was on industries with in situ wastewater treatment and direct discharge into receiving surface waters. Specifically, the effluents of two industrial plants in the field of surface treatment, two in the paper and pulp sector, two of the food industry, two thermal power plants, one petrochemical industry, and one plant of steel production were analysed. For each industrial WWTP, proportional weekly composite samples were collected twice. The analysis in this case targeted the whole spectrum of examined substances (Table 2).

2.2. Samples handling and chemical analysis

Most water samples, namely river water, municipal and industrial wastewater effluents, and bulk deposition were collected in high density polyethylene (HDPE) bottles or canisters, which were previously thoroughly flushed with the sampling matrix. For groundwater, samples were collected in pre-cleaned glass bottles ranging from 100 ml to 2 l, depending on the targeted parameters. All samples were cooled and transported to the analysing laboratory within 24 h. Samples that needed to be preserved for their later combination were immediately frozen at -20° upon receipt in the laboratory. Samples for which filtration was required were filtered through a $0.45\ \mu\text{m}$ filter within 24 h upon receipt in the laboratory and prior to their freezing. Fresh SPM and composite soil samples were cooled at 4° until their lyophilisation. Lyophilised samples were stored in HDPE containers and analysed within three months. All chemical analyses were performed by ISO/IEC 17025 accredited laboratories according to national or international validated standard procedures. Table 2 reports the specific procedures applied for the analysis as well as their LOQ and LOD (when available). Details regarding the methods followed for the preparation and preconcentration of the samples and the instrumentation employed to perform the analyses are reported in Appendix D.1. Given the difficulty of measuring very low concentrations of pollutants in largely different matrices, a strict quality control was applied to the whole spectrum of chemical analyses, including replicates, determination of blanks and determination of specific recoveries. Appendix D.2 and Appendix D.3 report recoveries obtained for each compound in the different sample matrices as well as the standards used to determine them. Further, Appendix D.4 and Appendix D.5 report examples of chromatograms for PBDE and PAH analyses both in standard solutions and in different types of samples. They show that despite the visible negative effect exerted by different matrices on the precision of the analysis, peaks corresponding to different PBDE congeners and PAH compounds were still clearly distinguishable. With respect to the limits of quantification, they were calculated for each sample and compound by taking into account not only the given limits of quantification of the employed instrumentation, but also sample-specific influence, such as matrix effects and preconcentration steps, blank values and dry weight (for solid samples). The LOQ values given in Table 2 represent the limits generally achieved in most of the analysed samples. Any measurement that did not meet high standards of accuracy and plausibility during the whole process of quality control was discarded and no quantitative result was provided.

2.3. Data analysis

In the data evaluation, measurements below the LOQ were assigned the mean value between LOD and LOQ, whereas non-detects were

Table 2

List of analysed contaminants and applied analytical methods with corresponding Limits of Quantification (LOQ) and Limits of Detection (LOD). When limits differ for specific matrices, ranges are given.

| Group | Parameter | Water samples | | | Solid samples | | |
|------------|-----------|------------------------------|------------------------------|------------------|-------------------------------|-------------------------------|--------------------|
| | | LOQ [$\mu\text{g l}^{-1}$] | LOD [$\mu\text{g l}^{-1}$] | Method | LOQ [$\mu\text{g kg}^{-1}$] | LOD [$\mu\text{g kg}^{-1}$] | Method |
| Metals | Hg | 0.0001–0.001 | na-0.0005 | DIN EN 13506-E35 | 10 | na | DIN EN 13506-E35 |
| Metals | Cd | 0.001–0.05 | na-0.025 | DIN 38406-29-E29 | 100 | na | DIN 38406-29-E29 |
| Metals | Pb | 0.01–0.5 | na-0.1 | DIN 38406-29-E29 | 1000 | na | DIN 38406-29-E29 |
| Metals | Ni | 0.01–4 | na-1 | DIN 38406-29-E29 | 1000 | na | DIN 38406-29-E29 |
| Metals | Cu | 0.01–1 | na-0.1 | DIN 38406-29-E29 | 10000 | na | DIN 38406-29-E29 |
| Metals | Zn | 0.01–1 | na-0.2 | DIN 38406-29-E29 | 10000 | na | DIN 38406-29-E29 |
| Organotins | MBT | 0.008 | 0.004 | DIN EN ISO 17353 | 2 | 1 | ÖNORM EN ISO 23161 |
| Organotins | DBT | 0.0002 | 0.0001 | DIN EN ISO 17353 | 2 | 1 | ÖNORM EN ISO 23161 |
| Organotins | TBT | 0.0002 | 0.0001 | DIN EN ISO 17353 | 2 | 1 | ÖNORM EN ISO 23161 |
| Organotins | TeBT | 0.0002 | 0.0001 | DIN EN ISO 17353 | 2 | 1 | ÖNORM EN ISO 23161 |
| Organotins | DPhT | 0.0002 | 0.0001 | DIN EN ISO 17353 | 2 | 1 | ÖNORM EN ISO 23161 |
| Organotins | TPhT | 0.0002 | 0.0001 | DIN EN ISO 17353 | 2 | 1 | ÖNORM EN ISO 23161 |
| PAHs | NAP | 0.002–0.0074 | 0.001–0.002 | DIN 38407-39 | 7.2 | 2 | ÖNORM L1200 |
| PAHs | ACY | 0.0015–0.0025 | 0.00075–0.00077 | DIN 38407-39 | 4.3 | 1.1 | ÖNORM L1200 |
| PAHs | ACE | 0.0005–0.0025 | 0.0002–0.0015 | DIN 38407-39 | 4.5 | 1.3 | ÖNORM L1200 |
| PAHs | FLN | 0.0005–0.0025 | 0.0002–0.0015 | DIN 38407-39 | 6.9 | 2 | ÖNORM L1200 |
| PAHs | PHE | 0.0005–0.0025 | 0.0002–0.00064 | DIN 38407-39 | 4 | 1.1 | ÖNORM L1200 |
| PAHs | ANT | 0.001–0.018 | 0.00049–0.0005 | DIN 38407-39 | 1.3 | 0.29 | ÖNORM L1200 |
| PAHs | FLT | 0.001–0.005 | 0.0005–0.0022 | DIN 38407-39 | 4.3 | 1.2 | ÖNORM L1200 |
| PAHs | PYR | 0.0005–0.0025 | 0.0002–0.00088 | DIN 38407-39 | 4 | 1.2 | ÖNORM L1200 |
| PAHs | BAA | 0.0012–0.0025 | 0.00019–0.0006 | DIN 38407-39 | 7.5 | 2.3 | ÖNORM L1200 |
| PAHs | CHR | 0.001–0.0025 | 0.0005–0.00057 | DIN 38407-39 | 6.6 | 1.9 | ÖNORM L1200 |
| PAHs | BBF | 0.001–0.0011 | 0.0005–0.00086 | DIN 38407-39 | 8.3 | 2.5 | ÖNORM L1200 |
| PAHs | BKF | 0.001–0.0011 | 0.00044–0.00055 | DIN 38407-39 | 6.2 | 2 | ÖNORM L1200 |
| PAHs | BAP | 0.001 | 0.0004–0.0005 | DIN 38407-39 | 4.8 | 1.2 | ÖNORM L1200 |
| PAHs | BPE | 0.001–0.0015 | 0.00042–0.00075 | DIN 38407-39 | 6.6 | 2 | ÖNORM L1200 |
| PAHs | DHA | 0.0012–0.0025 | 0.00037–0.0006 | DIN 38407-39 | 4.2 | 1.2 | ÖNORM L1200 |
| PAHs | IPY | 0.001–0.0015 | 0.00038–0.00075 | DIN 38407-39 | 3.6 | 1 | ÖNORM L1200 |
| PBDEs | BDE-28 | 0.0001-na | na-0.00001 | DIN EN ISO 22032 | 0.0013–0.0021 | 0.00065–0.001 | EPA 1614 |
| PBDEs | BDE-47 | 0.0001-na | na-0.00001 | DIN EN ISO 22032 | 0.031–0.038 | 0.015–0.019 | EPA 1614 |
| PBDEs | BDE-99 | 0.0001-na | na-0.00016 | DIN EN ISO 22032 | 0.014–0.025 | 0.0068–0.012 | EPA 1614 |
| PBDEs | BDE-100 | 0.0001-na | na-0.000034 | DIN EN ISO 22032 | 0.0032–0.0055 | 0.0016–0.0027 | EPA 1614 |
| PBDEs | BDE-153 | 0.0001-na | na-0.00016 | DIN EN ISO 22032 | 0.00048–0.0018 | 0.00024–0.00092 | EPA 1614 |
| PBDEs | BDE-154 | 0.0001-na | na-0.000011 | DIN EN ISO 22032 | 0.00083–0.0028 | 0.00041–0.0014 | EPA 1614 |
| PFAAs | PFOS | 0.001 | na-0.0005 | DIN 38407-F42 | 0.5–0.7 | 0.25–0.35 | DIN CEN/TS 15968 |
| PFAAs | PFOA | 0.001 | na-0.0005 | DIN 38407-F42 | 0.5–0.7 | 0.25 | DIN CEN/TS 15968 |

Note: The preparation of solid samples for the analysis of metals was performed according to the standard DIN EN 13346.

considered equal to zero. As shown in Table 2, for some parameters and matrices only information on LOQ is available and no distinction could therefore be made between non-detectable (n.d.; <LOD) and non-quantifiable (n.q.; < LOQ). In these cases, results below the LOQ were set equal to half of it. The first part of the analysis aimed to gain an overview of average concentrations in specific environmental and engineered compartments. In addition to presenting and discussing the concentration levels in SPM, these were also used to estimate particulate concentrations in the water phase, in order to enable a direct comparison with the measurements related to the dissolved phase. This estimation, based on the measured concentration of the pollutants in SPM and the mean SPM concentration measured during the studied period, was carried out for the catchments where continuous or high resolution measurements of SPM concentrations were available (namely HOAL, Wulka, Raba, Ötztaler Ache and Dornbirnerach). Given the high variability of SPM concentration over time, this analysis has restricted accuracy and significance and does not illustrate the peaks of particulate transport during storm events, but it provides nevertheless a useful information on the order of magnitude of this transport pathway at average conditions. Results aggregated by compounds and compartments are presented in Sections 3.1 and 3.2, where they are also discussed in the context of international literature. For the sake of comparability, studies referring to heavily polluted, urbanized and industrialized catchments or to geographically very distant areas, as well as studies conducted more than 15 years ago, were not considered. In addition, Appendix A relates the results with Environmental Quality Standards in surface water bodies (GBL II Nr. 96, 2006) and in

groundwater (BGBl. II Nr. 98, 2010) as well as with precautionary limits in agricultural soils (ÖNORM L 1075, 2017). In a second step, data were analysed in more detail to investigate specific relationships between and within compartments. First, for the nine study catchments, mean concentration values at baseflow were compared to mean concentration levels at high flow. Second, for the three catchments in which arable land dominates as land-use and where arable soil was analysed (HOAL, Pram, Wulka), mean concentration values in SPM were compared to mean concentration level in soil, to shed light on the emissions via agricultural erosion and on the potential enrichment of contaminants through particulate transport. Third, a bootstrap analysis for the difference between medians (Efron and Tibshirani, 1993) was performed in R (R Core Team, 2013) to deeper examine concentration levels of contaminants in wastewater effluents. Data were subdivided into four groups: small (20,000–50,000 $\text{PE}_{\text{COD}120}$), medium (50,000–150,000 $\text{PE}_{\text{COD}120}$) and large municipal WWTPs (>150,000 $\text{PE}_{\text{COD}120}$), and industrial WWTPs. Samples of differences between median concentration values were randomly generated for each couple or combination of groups (1,000 resamples). Confidence intervals of the resulting distributions were successively analysed to test the significance of the differences between medians. Results of these analyses are presented in detail in Appendix B and Appendix C and they are discussed for specific contaminants within Sections 3.1 and 3.2.

Table 3
PAH₁₆ concentration levels in environmental and engineered compartments. Compounds are listed in order of increasing molecular weight and hydrophobicity.

| | Filtered stream water | | SPM | | Soil | | Bulk deposition | | Groundwater | | Municipal WWTP effluent | | Industrial WWTP effluent | |
|--------------------|--------------------------------------|----------------------|--|----------------------|---|----------------------|---|----------------------|---|----------------------|---|----------------------|---|----------------------|
| | Mean-Median [µg l ⁻¹] | n.d.- n.q. (n) | Mean-Median (Min-Max) [µg kg ⁻¹] | n.d.- n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.- n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.- n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.- n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.- n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.- n.q. (n) |
| NAP | 0.014–0.013 (0.0027–0.041) | 0-0 (36) | <7.2–<7.2 (<2–28) | 5-12 (26) | 18-11 (<1.1–66) | 1-1 (26) | 0.012–0.0096 (0.0033–0.028) | 4-9 (18) | 0.015–<0.0020 (<0.0010–0.34) | 57-17 (125) | 0.011–0.010 (<0.0020–0.054) | 8-6 (31) | 0.026–0.022 (<0.0020–0.059) | 0-1 (18) |
| ACY | <0.00075–<0.00075 | 36-0 (36) | <4.3–<4.3 (<1.1–13) | 6-13 (26) | <4.3–<4.3 (<1.1–13) | 3-11 (18) | <0.00075–<0.00075 (<0.00075–0.0022) | 13-1 (15) | <0.0077–<0.00077 (<0.00077–0.0049) | 120-1 (125) | <0.0025–<0.0025 (<0.00076–0.0059) | 11-7 (31) | <0.0075–<0.00075 (<0.00075–0.0017) | 13-4 (18) |
| ACE | 0.0049–0.0022 (<0.00025–0.024) | 6-5 (36) | <4.5–<4.5 (<1.3–8.4) | 6-16 (26) | <1.3–<1.3 (<1.3–<4.5) | 16-2 (18) | 0.0012–0.00063 (<0.00025–0.0042) | 2-5 (15) | <0.0020–<0.00020 (<0.00020–0.0049) | 119-3 (125) | <0.0025–<0.0025 (<0.0015–0.0079) | 15-8 (31) | 0.013–0.014 (<0.00025–0.029) | 1-1 (18) |
| FLN | 0.0053–0.0029 (<0.00025–0.024) | 2-7 (36) | <6.9–<6.9 (<2.0–<6.9) | 4-12 (26) | <2.0–<2.0 (<2.0–<6.9) | 12-6 (18) | 0.0013–0.00055 (<0.00025–0.0040) | 4-2 (15) | <0.0050–<0.00020 (<0.00020–0.013) | 102- (125) | <0.0025–<0.0015 (<0.0015–0.0073) | 18-2 (31) | 0.012–0.012 (<0.00025–0.048) | 1-0 (18) |
| PHE | 0.011–0.011 (0.0051–0.045) | 0-0 (36) | 46.52 (<4–88) | 0-1 (26) | 18-11 (<1.1–66) | 1-1 (26) | 0.0038–0.0014 (0.00025–0.014) | 1-1 (18) | 0.0016–<0.0005 (<0.00020–0.058) | 56-23 (125) | 0.0042–0.0034 (<0.00064–0.019) | 8-7 (31) | 0.016–0.015 (<0.00050–0.029) | 0-1 (18) |
| ANT | <0.00050–<0.00050 | 26-5 (36) | 6.5–5.5 (<0.29–16) | 2-3 (26) | 3.7–2.6 (<0.0050–<0.00050) | 1-3 (18) | <0.00050–<0.00050 (<0.00050–0.0011) | 12-2 (15) | <0.0010–<0.00050 (<0.00050–0.0045) | 112-4 (125) | <0.018–<0.00049 (<0.00049–<0.018) | 29-2 (31) | <0.0050–<0.00050 (<0.00050–0.0020) | 14-3 (18) |
| FLT | <0.0010–<0.0010 | 13-9 (36) | 72.58 (<1.2–200) | 1-1 (26) | 55-30 (<0.29–9.7) | 0-0 (18) | 0.0014–<0.0010 (<0.00050–0.0070) | 4-5 (15) | <0.0010–<0.00050 (<0.00050–0.017) | 108-7 (125) | <0.0022–<0.0022 (<0.00022–<0.0050) | 30-1 (31) | <0.0010–<0.0010 (<0.00050–0.0036) | 9-4 (18) |
| PYR | 0.0064–0.0056 (<0.00025–0.0022) | 10-7 (36) | 63.43 (<1.2–170) | 1-1 (26) | 42-24 (5.0–150) | 0-0 (18) | 0.0011–<0.00059 (<0.00025–0.0069) | 3-4 (15) | 0.0068–<0.00020 (<0.00020–0.018) | 84-18 (125) | <0.0088–<0.00088 (<0.00088–0.0039) | 28-2 (31) | 0.0056–<0.00050 (<0.00025–0.0019) | 8-3 (18) |
| BAA | <0.00060–<0.00060 | 35-1 (36) | 43-37 (<2.3–130) | 3-2 (26) | 29-17 (<2.3–100) | 1-3 (18) | <0.0012–<0.00060 (<0.00060–0.0089) | 12-1 (15) | <0.0050–<0.00050 (<0.00050–0.0080) | 112-5 (125) | <0.00019–<0.00019 (<0.00019–<0.0025) | 28-3 (31) | <0.0060–<0.00060 (<0.00060–<0.00060) | 18-0 (18) |
| CHR | <0.00050–<0.00050 | 35-0 (36) | 52-48 (<1.9–140) | 2-3 (26) | 35-20 (<1.9–98) | 1-0 (18) | <0.0010–<0.00050 (<0.00050–0.0092) | 12-0 (15) | <0.0010–<0.00050 (<0.00050–0.036) | 115-0 (125) | <0.00057–<0.00057 (<0.00057–0.0025) | 27-3 (31) | <0.0050–<0.00050 (<0.00050–<0.0010) | 17-1 (18) |
| BBF | <0.00055–<0.00055 | 35-1 (36) | 38-36 (<2.5–110) | 3-2 (26) | 34-19 (<2.5–92) | 1-3 (18) | <0.0011–<0.00055 (<0.00055–0.0098) | 11-0 (15) | <0.0050–<0.00050 (<0.00050–0.0075) | 115-3 (125) | <0.00086–<0.00086 (<0.00086–0.0032) | 29-1 (31) | <0.0050–<0.00055 (<0.00055–<0.0011) | 16-2 (18) |
| BKF | <0.00055–<0.00055 | 36-0 (36) | 22-20 (<2.0–63) | 4-1 (26) | 16-8.3 (<2.0–46) | 1-4 (18) | <0.0011–<0.00055 (<0.00055–0.0050) | 11-2 (15) | <0.0050–<0.00050 (<0.00050–0.0048) | 118-2 (125) | <0.00044–<0.00044 (<0.00044–<0.0040) | 29-0 (31) | <0.0055–<0.00055 (<0.00055–<0.00055) | 18-0 (18) |
| BAP | <0.00050–<0.00050 | 36-0 (36) | 37-28 (<1.2–110) | 2-2 (26) | 26-16 (<4.8–89) | 0-3 (18) | <0.0010–<0.00050 (<0.00050–0.012) | 12-0 (15) | <0.0050–<0.00050 (<0.00050–0.0074) | 115-5 (125) | <0.00040–<0.00040 (<0.00040–<0.0029) | 29-1 (31) | <0.0050–<0.00050 (<0.00050–<0.00050) | 18-0 (18) |
| BPE | <0.00075–<0.00075 | 36-0 (36) | 31-27 (<2.0–82) | 2-3 (26) | 21-13 (<6.6–58) | 0-3 (18) | <0.0015–<0.00075 (<0.00075–0.0082) | 12-1 (15) | <0.0042–<0.00042 (<0.00042–0.014) | 115-6 (125) | <0.00059–<0.00059 (<0.00059–0.013) | 28-1 (31) | <0.0075–<0.00075 (<0.00075–<0.00075) | 18-0 (18) |
| DHA | <0.00060–<0.00060 | 36-0 (36) | 8.3–6.9 (<1.2–24) | 5-4 (26) | 6.3–2.7 (<1.2–20) | 2-8 (18) | <0.0060–<0.00060 (<0.00060–0.0025) | 13-0 (15) | <0.0037–<0.00037 (<0.00037–<0.0036) | 116-6 (125) | <0.0025–<0.00047 (<0.00047–<0.018) | 28-2 (31) | <0.0060–<0.00060 (<0.00060–<0.00060) | 18-0 (18) |
| IPY | <0.00075–<0.00075 | 36-0 (36) | 28-22 (<1.0–80) | 2-3 (26) | 21-12 (<3.6–58) | 0-2 (18) | <0.0015–<0.00075 (<0.00075–0.0082) | 12-0 (15) | <0.0038–<0.00038 (<0.00038–0.011) | 115-5 (125) | <0.0057–<0.00057 (<0.00057–0.0022) | 27-2 (31) | <0.0075–<0.00075 (<0.00075–<0.00075) | 18-0 (18) |
| ΣPAH ₁₆ | 0.038–0.031 (0.0048–0.13) | - (36) | 470-420 (7.0–1150) | - (26) | 320-180 (21–1005) | - (18) | 0.027–0.022 (0.0033–0.10) | - (15) | 0.020–0.0025 (<LOD–0.36) | - (125) | 0.023–0.015 (<LOD–0.074) | - (31) | 0.069–0.065 (0.0052–0.14) | - (18) |

Note: Measured values (in case of minimum or maximum) and calculated values (in case of mean and median) below LOD or below LOQ, are indicated as smaller than the respective specific analytical limits.

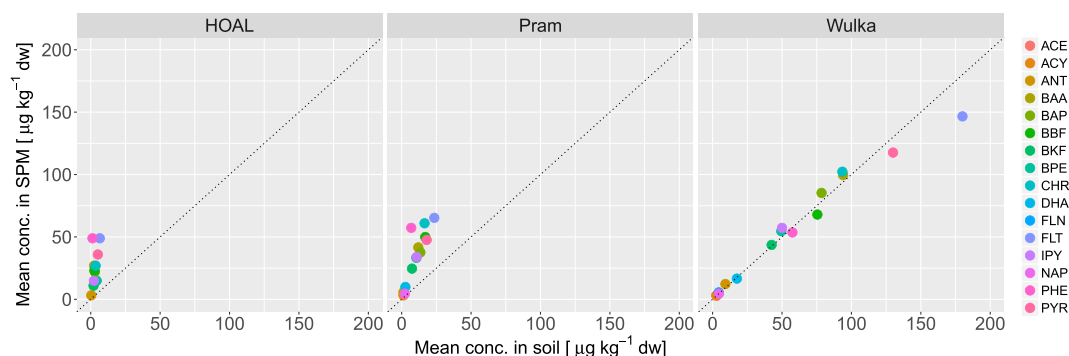


Fig. 2. Relationship between mean concentrations of PAH compounds in SPM and in arable soil in three predominantly agricultural catchments. Note: values are not displayed for compounds below the LOD in soil.

3. Results and discussion

3.1. Organic compounds

3.1.1. Polycyclic aromatic hydrocarbons

The sixteen PAHs examined in this study are characterized by a gradient of molecular weight and hydrophobicity, which is well reflected in their varying occurrence in different environmental and engineered compartments (Table 3). The low molecular weight compounds (two-three aromatic rings, i.e. NAP, ACY, ACE, FLN, PHE, and ANT) were, with the exception of ACY and ANT, detectable and/or quantifiable in most samples of filtered stream water and bulk deposition. Among them, NAP and PHE present highest levels, with median of $0.013 \mu\text{g l}^{-1}$ and $0.011 \mu\text{g l}^{-1}$ in filtered river water and of $0.0096 \mu\text{g l}^{-1}$ and $0.0014 \mu\text{g l}^{-1}$ in bulk deposition, respectively. These two compounds are also the only ones with a considerable occurrence in the examined groundwaters, with approximately 35–40% of the measurements above the LOQ and mean values of $0.015 \mu\text{g l}^{-1}$ (NAP) and $0.0016 \mu\text{g l}^{-1}$ (PHE). All other PAHs were n.d. in the majority of groundwater samples. Among the high molecular weight compounds, FLT and PYR (four aromatic rings) were also often found in river water and bulk deposition samples, although in the dissolved phase of rivers they present concentration levels one or even two orders of magnitude lower than the low molecular weight compounds. The remaining eight PAHs were almost systematically n.d. in filtered stream water and in bulk deposition, most likely due to their high octanol-water partitioning coefficients ($\log K_{OW}$) above 5.6. Publicly available studies on occurrence and distribution of PAHs are predominantly focused on heavily urbanized or industrialized areas, which are profoundly different from the case-studies selected here. Nevertheless, if related e.g. to the investigations conducted in relatively comparable French rivers by Net et al. (2014) and Chiffre et al. (2015), the levels of $\sum \text{PAH}_{16}$ measured in this study fall into the lowest level of published ranges. In fact, whereas in this study the sum parameter $\sum \text{PAH}_{16}$ in the dissolved water column presents a median of $0.031 \mu\text{g l}^{-1}$ and a range between 0.0048 and $0.13 \mu\text{g l}^{-1}$, Net et al. (2014) and Chiffre et al. (2015) reported an average of $0.28 \mu\text{g l}^{-1}$ and the range 0.074 – $0.73 \mu\text{g l}^{-1}$, respectively. In good agreement with these studies is the pronounced dominance of two and three-ring compounds in the dissolved water phase. High sorption capacity is, together with chemical stability, one of the characteristics that make PAHs very persistent in the environment. This property is well visible in the analysis of SPM and soil, in which both low and high molecular weight compounds were found in a broad range of concentration levels. The only river with very low values for all PAH_{16} in SPM (mostly n.d. or n.q.) is the one predominantly fed by a glacier (Ötztaler Ache). Whereas two and three-rings compounds present medians below $7.2 \mu\text{g kg}^{-1}\text{dw}$ both in SPM and soil, compounds with higher molecular weight have median levels above $20 \mu\text{g kg}^{-1}\text{dw}$ in SPM and above $8 \mu\text{g kg}^{-1}\text{dw}$ in soil. Two exceptions are PHE and DHA,

which present higher and lower levels than their groups, respectively. Most relevant compounds in SPM are PHE, FLT, PYR, BAA, BBF and CHR. This depicts a pattern very similar to the one reported by Chiffre et al. (2015). The results for the sum parameter $\sum \text{PAH}_{16}$ in SPM, with a median of $420 \mu\text{g kg}^{-1}\text{dw}$ and a maximum value of $1150 \mu\text{g kg}^{-1}\text{dw}$, are aligned, in their order of magnitude, with the levels reported for rivers in France and Germany, although they are lower. Higher ranges were in fact reported by Chiffre et al. (2015) (750 – $2500 \mu\text{g kg}^{-1}\text{dw}$), Le Meur et al. (2017) (2300 – $7700 \mu\text{g kg}^{-1}\text{dw}$), Wölz et al. (2010) (1000 – $5000 \mu\text{g kg}^{-1}\text{dw}$), and Abuhelou et al. (2017) (1300 – $39,000 \mu\text{g kg}^{-1}\text{dw}$). A much more similar range, namely 230 – $1030 \mu\text{g kg}^{-1}\text{dw}$, was measured by Countway et al. (2003) in the York River, a subestuary of the Chesapeake Bay. The main reason for the observed differences might lie in the focus of the present work on either background situations or on catchments with low or null wastewater discharges. As far as soils are concerned, the level of $\sum \text{PAH}_{16}$ measured in background forest soils (median $270 \mu\text{g kg}^{-1}\text{dw}$; maximum $590 \mu\text{g kg}^{-1}\text{dw}$) falls in the lower range of the average concentrations reported for forest and mountainous areas in other European countries, which vary between 400 and $2100 \mu\text{g kg}^{-1}\text{dw}$ (Aichner et al., 2013; Schwarz et al., 2011; Quiroz et al., 2011; Bosch et al., 2015). Concentrations of $\sum \text{PAH}_{16}$ in arable soils show highest variability, with values comprised between 21 and $1005 \mu\text{g kg}^{-1}\text{dw}$. As in the case of forest soils, these levels are in the lower range of the results reported in the literature. Taking again Germany as comparison due to its geographical and climatic similarity to Austria, Schwarz et al. (2011) reported a median level of $\sum \text{PAH}_{16}$ in agricultural soils equal to $1288 \mu\text{g kg}^{-1}\text{dw}$.

As shown in Fig. 2 and detailed in Appendix B, the comparison between mean concentration levels in arable soil and in SPM depicts different patterns among the examined catchments with land-use dominated by arable land. In accordance with previous findings (Zheng et al., 2012), results in the HOAL and Pram catchments suggest a clear enrichment of PAHs, with factors ranging for most compounds between 2 and 8, although peak differences up to factor 38 were recorded. A very different situation emerges however for the catchment of the Wulka river. Here, both compartments contain considerably higher levels of PAHs (up to $180 \mu\text{g kg}^{-1}$), but no significant enrichment seems to take place.

It is interesting to observe that all PAH_{16} are present at measurable levels in soils, although many of them, especially the high molecular compounds, were largely n.d. in bulk deposition. Given the recalcitrance of PAHs in soils (Posada-Baquero and Ortega-Calvo, 2011), this discrepancy could be explained with the legacy of past atmospheric deposition. In the case of agricultural soils, however, the presence of PAHs could also potentially derive from application of sewage sludge, compost and digestates (Stefaniuk et al., 2018; Clara et al., 2016; Wiechmann et al., 2013; Stäb, 2011; Kupper, 2008; Kupper and Fuchs, 2007; Scheffknecht, 2005). With respect to municipal wastewater

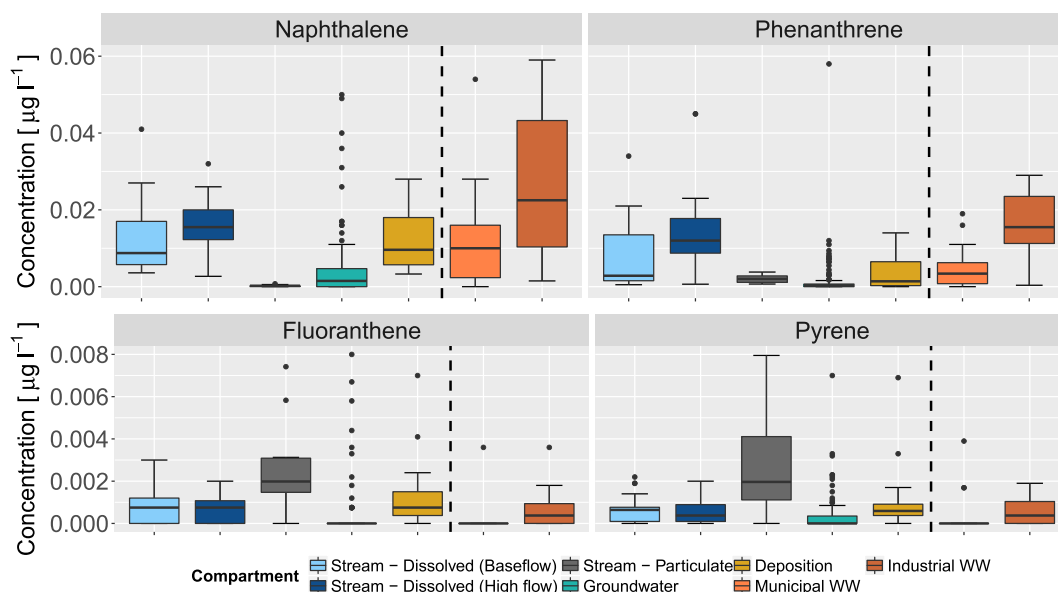


Fig. 3. Concentration of selected PAHs in environmental and engineered compartments. Lower and upper hinges correspond to first and third quartiles. Values beyond the range of $1.5 \times \text{IQR}$ (inter-quartile range) are plotted individually. Values for the stream particulate phase are estimations derived from concentrations in SPM and related to mean SPM transport. Sample size varies considerably between compartments (see Table 3). To make the graph more readable, extreme outlying values measured in groundwater are not depicted.

effluents, only the five low molecular weight compounds NAP, ACY, ACE, FLN, and PHE were present in measurable levels. With a median value of $0.01 \mu\text{g l}^{-1}$, levels of NAP are one order of magnitude higher than those of other compounds. This is in line with the findings of Chiffre et al. (2015), who reported a pronounced abundance of low molecular PAH in effluents of French municipal WWTPs. The level of the sum parameter $\sum \text{PAH}_{16}$ (median of $0.015 \mu\text{g l}^{-1}$) is however smaller than the range measured by Chiffre et al. (2015), namely $0.085\text{--}0.313 \mu\text{g l}^{-1}$, which in turn was considerably lower than other values reported e.g. for Chinese, Canadian or Italian WWTPs. Similarly, effluents of industrial plants show measurable levels only for PAHs with up to four aromatic rings. Major compounds in this compartment are NAP, ACE, FLN, and PHE, with median concentrations comprised in the range $0.012\text{--}0.022 \mu\text{g l}^{-1}$. As reported in Appendix C (Table C.17), industrial effluents contain significantly higher levels of NAP, ACE, FLN, and PHE, whereas measured concentrations of ACY are higher in municipal effluents. Fig. 3 illustrates the distribution of selected PAHs in the different compartments. The low molecular NAP and PHE, on the top row of the figure, are predominantly transported in rivers in the dissolved phase, whereas for 4-rings FLT and PYR, on the bottom row, particulate transport visibly plays a dominant role. It can be observed that levels of NAP and PHE in bulk deposition and municipal WWTP effluents are similar to those measured in the dissolved phase of rivers. For FLT and PYR, ranges found in rivers and in deposition are similar to those in industrial WWTP effluents and much higher than those in municipal effluents. These findings confirm the still current relevance of atmospheric deposition as direct and indirect emission pathway for selected PAHs.

3.1.2. Polybrominated diphenyl ethers

Similarly to high molecular weight PAHs, PBDE compounds are hydrophobic and tend to be adsorbed to particles rather than be in the dissolved phase. Indeed, in filtered stream water samples, all congeners were systematically below $0.0001 \mu\text{g l}^{-1}$ (Table 4). Bulk deposition and groundwater revealed the very same pattern. On the contrary, they were present in most samples of soil and SPM. Fig. 5 shows the normalised relative distribution of the six examined congeners in these two compartments. Despite a few exceptions and fluctuations, the distribution of congeners within each compartment is quite similar and

shows a clear dominance of BDE-47 (median relative abundance in soil: 43% and in SPM: 40%) and BDE-99 (median relative abundance in soil: 32% and in SPM: 40%). These results correspond quite well with the ratio of congeners in typical penta-BDE technical products (BDE-47: 38–43%; BDE-99: 45–49%; BDE-100: 8–13%; BDE-153: 5.3–5.4%; BDE-154: 2.7–4.5%) (Arellano et al., 2014; La Guardia et al., 2006). The sometimes lower relative abundance of BDE-99 might be explained with its partial natural degradation into lower brominated BDEs. Among soils, the highest values were found in background forests, with $\sum \text{BDE}_6$ presenting a median level of $0.15 \mu\text{g kg}^{-1} \text{dw}$ and a maximum of $1.4 \mu\text{g kg}^{-1} \text{dw}$. Arable and grassland soils present much lower median values of 0.067 and $0.078 \mu\text{g kg}^{-1} \text{dw}$, respectively, although for grassland soils also a maximum level of $0.95 \mu\text{g kg}^{-1} \text{dw}$ was measured. These results correspond well with investigations performed in other countries. Sellström et al. (2005) reported the range of $0.03\text{--}0.84$ for $\sum \text{BDE}_6$ in agricultural soils in Sweden, whereas Schuster et al. (2011) published the range $0.0029\text{--}1.8 \mu\text{g kg}^{-1} \text{dw}$ for $\sum \text{BDE}_6$ in remote rural woodland and grassland in the UK and in Norway. Similarly to what was observed for high molecular PAH compounds, PBDEs are present in soils although they are almost systematically n.d. in bulk deposition (only BDE-47 and BDE-99 were found in one sample). As for PAHs, it can be hypothesized that their presence in soils is due to the legacy of higher atmospheric deposition rates in the past or also potentially to the application of sewage sludge (Akortia et al., 2016). With respect to SPM, a comparison with the literature is very difficult due to the paucity of publications presenting the analysis of PBDE content in SPM in areas relatively similar to the catchments object of this work. Two studies performed in the Netherlands, one before and the other after the introduction of restrictive legislation in the EU, both reported ranges of PBDE in SPM which are at least one order of magnitude higher than those presented here (López et al., 2011; de Boer et al., 2003). Unlike the catchments of this work, however, the aquatic environments analysed by those two studies were more exposed to urban and industrial contamination. The recent and very exhaustive review of sources, levels, transport and toxicity of PBDEs by Akortia et al. (2016) does not cite any further study addressing this compartment, whereas sediment and biota have been extensively investigated. The comparison between mean concentration levels in arable soil and in SPM in the study catchments depicts for PBDEs a different pattern than the one described

Table 4
PBDE concentration levels in environmental and engineered compartments.

| | Filtered stream water | | | SPM | | | Soil | | | Bulk deposition | | | Groundwater | | | Municipal WWTP effluent | | | Industrial WWTP effluent | | |
|---------------------------|--|----------------------|--|---|----------------------|--|----------------------|--|----------------------|--|----------------------|--|----------------------|--|----------------------|--|----------------------|--|--------------------------|--|--|
| | Mean-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | (Min-Max) [$\mu\text{g kg}^{-1}$] | Mean-Median Max) [$\mu\text{g kg}^{-1}$] | n.d.- n.q. (n) | (Min-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | Mean-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | (Min-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | Mean-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | (Min-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | Mean-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | (Min-Median Max) [$\mu\text{g l}^{-1}$] | n.d.- n.q. (n) | | |
| BDE-28 | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 43 (43) | 0.0069–0.0058 (<0.0013–0.017) | <0.0021–<0.0021 (<0.00065–0.0092) | 2-12 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 16 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 22 (34) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | | |
| BDE-47 | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 43 (43) | 0.16–0.088 (<0.031–0.73) | 0.12–<0.038 (<0.015–0.67) | 1-10 (18) | 0.00064–<0.00010 (<0.00010–0.00028) | na- 15 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | 0.00011–<0.00027 (<0.00027–0.00098) | na- 27- (34) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | | |
| BDE-99 | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 43 (43) | 0.19–0.078 (<0.014–1.2) | 0.096–0.021 (<0.0068–0.47) | 0-8 (18) | 0.00054–<0.00010 (<0.00010–0.00012) | na- 15 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00016–<0.00016 (<0.00016–0.00048) | na- 24 (34) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | | |
| BDE-100 | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 43 (43) | 0.034–0.015 (<0.0032–0.20) | 0.024–0.0058 (<0.0032–0.12) | 0-5 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 16 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.000034–<0.000034 (<0.000034–0.00011) | na- 25- (34) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | | |
| BDE-153 | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 43 (43) | 0.016–0.0090 (<0.00024–0.099) | 0.014–0.0050 (<0.0048–0.053) | 0-1 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 16 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.000016–<0.000016 (<0.000016–0.000081) | na- 27- (34) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | | |
| BDE-154 | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 43 (43) | 0.024–0.0085 (<0.00041–0.14) | 0.023–0.0068 (<0.0083–0.14) | 0-1 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 16 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 123 (123) | <0.000011–<0.000011 (<0.000011–0.000028) | na- 25- (34) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | na- 18 (18) | | |
| Σ BDE ₆ | <LOQ - <LOQ (<LOQ - <LOQ) | - (43) | 0.43–0.21 (0.039–2.4) | 0.27–0.071 (0.018–1.4) | - (18) | 0.0031 - <LOQ (<LOQ-0.00053) | - (16) | <LOQ - <LOQ (<LOQ) | - (123) | <LOQ - <LOQ (<LOQ) | - (123) | 0.0022 - <LOD (<LOQ-0.0016) | - (34) | <LOQ - <LOQ (<LOQ) | - (18) | <LOQ - <LOQ (<LOQ) | - (18) | <LOQ - <LOQ (<LOQ) | - (18) | | |

Note: Measured values (in case of minimum or maximum) and calculated values (in case of mean and median) below LOD or below LOQ, are indicated as smaller than the respective specific analytical limits.

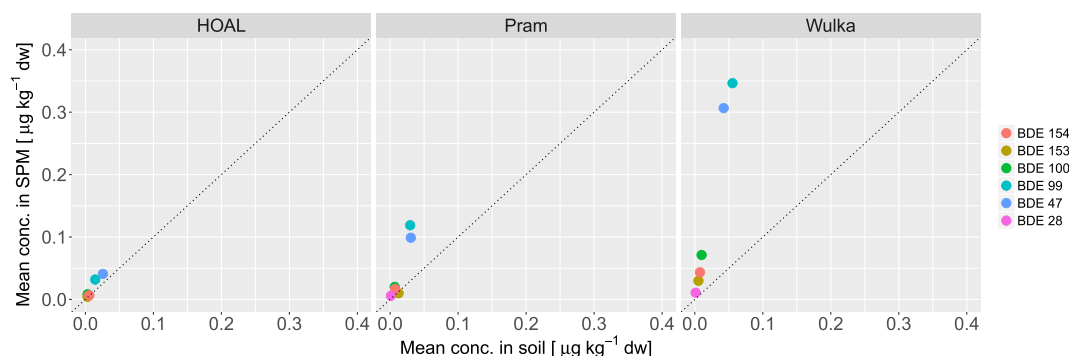


Fig. 4. Relationship between mean concentrations of PBDE compounds in SPM and in arable soil in three predominantly agricultural catchments. Note: values are not displayed for compounds below the LOD in soil.

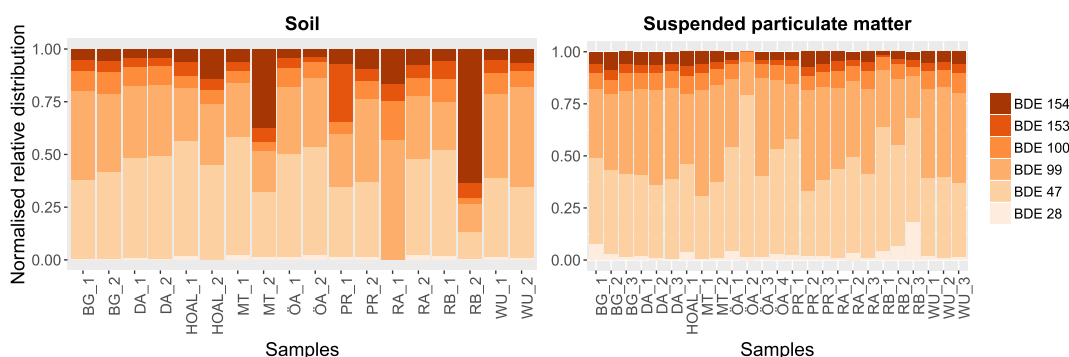


Fig. 5. Normalised relative distribution of six penta-BDE congeners in soil and suspended particulate matter. Samples refer to catchments'names, which are abbreviated as following: BG (Birkengraben), DA (Dornbirnerach), HOAL (HOAL), MT (Mattig), ÖA (Ötztaler Ache), PR (Pram), RA (Raba), RB (Reichramingbach), WU (Wulka).

for PAHs (Fig. 4 and in Appendix B). In this case, the arable soils of all three catchments contain similar concentration levels, but values in SPM diverge substantially. In particular, it is interesting to notice that for PBDEs it is the catchment of the Wulka river that shows the highest differences between SPM and soils (factors 6.3–8.5 for different congeners), whereas in the case of PAHs almost no enrichment was found in this catchment. Results for heavy metals and total phosphorus (TP), for which the enrichment process is partially better understood (Quinton and Catt, 2007), depict a more similar and consistent pattern in the three catchments (Tables 14, 15, 16). The factors calculated in this study cannot be considered as proper enrichment ratios, because these are usually derived from laboratory or field tests in which soil loss is directly measured and analysed. Values in SPM, instead, might also reflect the impact of other emission pathways. Nevertheless, this analysis shows the relevance and the need to further investigate the mechanisms of erosion for organic micropollutants at catchment scale.

As far as wastewater is concerned, PBDEs were not found in any of the industrial effluents. In municipal effluents, on the contrary, they were detectable in one quarter to a third of the samples, depending on the specific congeners. The mean level of BDE-47 was one to two orders of magnitude higher than the level of other congeners, whereas the second highest concentration level was measured for BDE-99. The range of the sum parameter $\sum \text{BDE}_6$, which varies from <LOQ to $0.0016 \mu\text{g l}^{-1}$, is lower, although in the same order of magnitude, than the findings of a previous Austrian survey reported by Clara et al. (2012).

3.1.3. Organotin

As shown in Table 5, three organotin compounds, namely TeBT, DPhT, and TPhT were systematically non detectable in all compartments, namely below $0.00010 \mu\text{g l}^{-1}$ in liquid samples and below $1 \mu\text{g kg}^{-1}\text{dw}$ in solid samples. Similarly, MBT was almost always below $0.0040 \mu\text{g l}^{-1}$ in industrial WWTP effluents, filtered stream water bulk

deposition and groundwater, and below $2 \mu\text{g kg}^{-1}\text{dw}$ in soil. The only exception was SPM, where MBT was the only examined organotin to be measurable in one third of the samples, with a maximum value of $1.5 \mu\text{g kg}^{-1}\text{dw}$. Generally, all butyltin compounds present a high tendency to be bound to particulate matter. However, different dominant binding forces might explain the different results for MBT and the other compounds. In fact, whereas some organotins, such as TBT, are mainly bound through hydrophobic forces, mineral binding prevails for MBT (like for trace metals) (Smedes et al., 2000). DBT and TBT show on the contrary a quite widespread occurrence across compartments, which is illustrated in Fig. 6. DBT was above the LOQ in the dissolved water phase of rivers in 65% of the samples, with a median of $0.00034 \mu\text{g l}^{-1}$ and maximum of $0.0044 \mu\text{g l}^{-1}$. In groundwater, DBT was measurable in 35% of the samples, with a mean value of $0.00084 \mu\text{g l}^{-1}$, whereas in municipal and industrial WWTP effluents half of the samples contained a measurable level, with mean concentrations of $0.00032 \mu\text{g l}^{-1}$ and $0.00044 \mu\text{g l}^{-1}$, respectively. Among these compartments, it is however in groundwater that the values spread over the largest range, covering over two orders of magnitude. TBT was above the LOQ in 40% of filtered river samples, with a mean of $0.00034 \mu\text{g l}^{-1}$ and maximum of $0.0037 \mu\text{g l}^{-1}$. Unlike DBT, TBT was almost always n.d. in municipal WWTP effluents. In groundwater and in industrial WWTP effluents, it was measurable in 30% and in 18% of the samples, respectively, with a mean value below $0.00020 \mu\text{g l}^{-1}$. In a previous screening conducted in Austria by Clara et al. (2012), TBT was detectable in 60% of municipal effluent samples, with a median of $0.00010 \mu\text{g l}^{-1}$. It is interesting to observe that, despite the relatively limited occurrence, all aforementioned compartments show the presence of values in the range of the EQS established for surface water bodies (Table A.10). The vast majority of the literature dealing with these compounds focuses on marine and estuarine environments. When inland freshwater is addressed, it typically is to investigate concentration levels in sediments and biota in the proximity of harbours or chemical plants. Notwithstanding, Bancon-

Table 5
Organotins concentration levels in environmental and engineered compartments.

| | Filtered stream water | | SPM | | Soil | | Bulk deposition | | Groundwater | | Municipal WWTP effluent | | Industrial WWTP effluent | |
|------|--|---------------|--|---------------|---|---------------|---|---------------|---|----------------|---|---------------|---|---------------|
| | Mean-Median [µg l ⁻¹] | n.d.-n.q. (n) | Mean-Median (Min-Max) [µg kg ⁻¹] | n.d.-n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.-n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.-n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.-n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.-n.q. (n) | Mean-Median (Min-Max) [µg l ⁻¹] | n.d.-n.q. (n) |
| MBT | <0.0040–<0.0040 (<0.0040–<0.0080) | 40-3 (43) | <1.0–<1.0 (<1.0–<2.0) | 7-10 (26) | <0.0040–<0.0040 (<0.0040–<0.0080) | 15-3 (18) | <0.0040–<0.0040 (<0.0040–<0.031) | 14-2 (16) | <0.0040–<0.0040 (<0.0040–<0.031) | 122-4 (128) | na | na | <0.0040–<0.0040 (<0.0040–<0.0040) | 16-0 (16) |
| DBT | 0.00063–0.00034 (<0.00010–0.0044) | 8-7 (43) | <1.0–<1.0 (<1.0–<1.0) | 22-4 (26) | <0.00010–<0.00020 (<0.00010–0.00032) | 18-0 (18) | 0.00084–<0.00020 (<0.00010–0.032) | 7-8 (16) | 0.00084–<0.00020 (<0.00010–0.032) | 48-35 (128) | 0.00032–<0.00020 (<0.00010–0.0016) | 10-8 (34) | 0.00044–<0.00020 (<0.00010–0.0020) | 5-4 (17) |
| TBT | 0.00034–<0.00020 (<0.00010–0.0037) | 18-8 (43) | <1.0–<1.0 (<1.0–<1.0) | 26-0 (26) | <0.00010–<0.00010 (<0.00010–0.00053) | 18-0 (18) | <0.00020–<0.00010 (<0.00010–0.00010) | 11-2 (16) | <0.00020–<0.00010 (<0.00010–0.00010) | 66-24 (128) | <0.00010–<0.00010 (<0.00010–0.00035) | 32-1 (34) | <0.00020–<0.00010 (<0.00010–0.00043) | 10-4 (17) |
| TeBT | <0.00010–<0.00010 (<0.00010–<0.00010) | 43-0 (43) | <1.0–<1.0 (<1.0–<1.0) | 26-0 (26) | <0.00010–<0.00010 (<0.00010–<0.00010) | 18-0 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | 16-0 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | 128-0 (128) | na | na | <0.00010–<0.00010 (<0.00010–<0.00010) | 17-0 (17) |
| DPHT | <0.00010–<0.00010 (<0.00010–<0.00010) | 43-0 (43) | <1.0–<1.0 (<1.0–<1.0) | 26-0 (26) | <0.00010–<0.00010 (<0.00010–<0.00010) | 18-0 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | 16-0 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | 128-0 (128) | na | na | <0.00010–<0.00010 (<0.00010–<0.00010) | 17-0 (17) |
| TPHT | <0.00010–<0.00010 (<0.00010–<0.00010) | 43-0 (43) | <1.0–<1.0 (<1.0–<1.0) | 26-0 (26) | <0.00010–<0.00010 (<0.00010–<0.00010) | 18-0 (18) | <0.00010–<0.00010 (<0.00010–<0.00010) | 16-0 (16) | <0.00010–<0.00010 (<0.00010–<0.00010) | 128-0 (128) | na | na | <0.00010–<0.00010 (<0.00010–<0.00010) | 17-0 (17) |

Note: Measured values (in case of minimum or maximum) and calculated values (in case of mean and median) below LOD or below LOQ, are indicated as smaller than the respective specific analytical limits.

Montigny et al. (2004) and Bancon-Montigny et al. (2008) examined in France levels of organotins in rivers, groundwater wells and WWTP effluents. The concentrations measured in this study for the dissolved phase in rivers correspond well to the lower level of the range published by Bancon-Montigny et al. (2004) for butyltin, namely 0.0002–0.03 µg l⁻¹. Our results also fall within the range reported by Bancon-Montigny et al. (2008) for background contamination by total organotins in surface and groundwater, which ranged from 0.00051 µg l⁻¹ to 0.071 µg l⁻¹. As far as it concerns WWTP effluents, Bancon-Montigny et al. (2008) were unable to detect organotins in some WWTPs, but measured substantially higher concentrations in others, varying between 0.061 µg l⁻¹ and 0.43 µg l⁻¹. In general, it can be observed that the dissolved phase of rivers presents substantially higher occurrence and concentration levels of DBT and TBT than the other examined compartments. This might be an indication of direct contamination still taking place locally through the legacy of anti-fouling paints in boats, harbours, or other infrastructure or equipment within the water bodies.

3.1.4. Perfluoroalkyl acids

Dissolved PFAAs were found at least once in all rivers except in the Drava. According to the literature review of Zareitalabad et al. (2013), reported concentrations of PFOS and PFOA in surface water extend over more than seven orders of magnitude, but half of the samples fall within the range 0.0008–0.013 µg l⁻¹, with the median varying between 0.0028 and 0.0033 µg l⁻¹, depending on how values below the LOD are considered. The results of this study also fall within such range (Table 6 and Fig. 7). Highest values (with peaks of 0.011 µg l⁻¹ for PFOS and 0.0064 µg l⁻¹ for PFOA) were recorded in rivers with relatively smaller or dryer catchments and with existence of point discharges. Despite uncertainties related to the partitioning and dissipation kinetics of PFAAs, not only surface waters but also groundwater bodies will ultimately be the final sink for these compounds (Zareitalabad et al., 2013). In this study, concentrations in groundwater were below 0.0010 µg l⁻¹ in three quarters of the samples. In the rest, they were found however at mean levels similar to those measured in surface waters and even presented higher maximum values up to 0.014 µg l⁻¹ for PFOS and 0.011 µg l⁻¹ for PFOA. Although these results indicate the existence of local criticalities, they depict an overall less contaminated situation than the findings of the pan-European survey conducted in groundwater bodies by Loos et al. (2010), in which PFOS were found in more than 48% of the samples, with an average level of 0.0040 µg l⁻¹ and a maximum value of 0.13 µg l⁻¹, whereas PFOA were detected in more than 65% of the samples, with an average level of 0.0030 µg l⁻¹ and a maximum value of 0.039 µg l⁻¹. PFOS and PFOA possess both hydrophobic and hydrophilic properties. According to the findings of this study, however, they are predominantly transported in the dissolved phase (Fig. 7). In suspended particulate matter, in fact, PFOA were mostly non-detectable (below 0.25 µg kg⁻¹dw), whereas PFOS were measurable in approximately one third of the samples, with a maximum value recorded corresponding to 1.6 µg kg⁻¹dw. A similar result was published by Nguyen et al. (2017), who found that both in river and sea samples the contribution of Σ PFASs in the particulate phase was insignificant (<1%) in comparison to the aqueous phase. In soil, PFAAs were found in half of the samples, with median concentration levels below 0.70 µg kg⁻¹dw. As reviewed by Milinovic et al. (2015) and Zareitalabad et al. (2013), international publications on PFAAs concentrations in soil are sparse and partially focused on heavily contaminated locations, which makes an inter-comparison very difficult. Rankin et al. (2016), however, recently published the results of a North American and global survey, in which PFOS and PFOA turned out to be the most commonly detected analytes among 32 per/polyfluoroalkyl substances. Their concentrations up to 3.1 and 2.7 µg kg⁻¹dw, respectively, are in the same order of magnitude of the maximum values measured in this study, namely 10 µg kg⁻¹dw for PFOS and 2.2 µg kg⁻¹dw for PFOA. With respect to the relative importance of

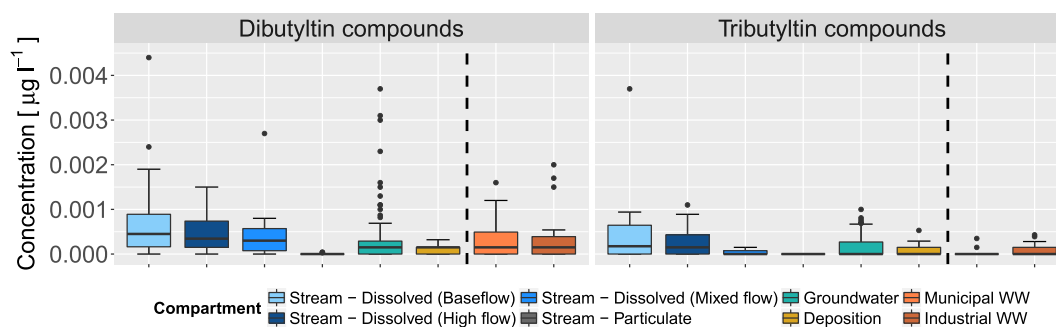


Fig. 6. Concentration of selected organotins in environmental and engineered compartments. Lower and upper hinges correspond to first and third quartiles. Values beyond the range of $1.5 \times \text{IQR}$ are plotted individually. The bar “Stream - Dissolved (Mixed flows)” relates to large rivers and river Zaya, for which composite samples collected at different flow conditions were analysed. Values for the stream particulate phase are estimations derived from concentrations in SPM and related to mean SPM transport. Sample size varies considerably between compartments (see Table 5).

different emission pathways for these compounds into water bodies, the international literature provides contrasting findings. Scott et al. (2010) and Filipovic et al. (2013), for instance, identified tributaries and precipitation as the dominant inputs of PFAAs into Lake Superior and Baltic Sea. On the contrary, according to Müller et al. (2011), loads of WWTP effluents and stormwater runoff were mostly responsible for the emission of these compounds within a small Swiss river catchment. As illustrated in Fig. 7, among all examined compartments PFOA presents the broadest range and the highest concentration levels in atmospheric bulk deposition. A higher median was calculated for municipal WWTP effluents, but due to the wide range of concentrations in deposition, it is not possible to distinguish among the two medians with statistical significance. This points to a varying potential importance of these two pathways in different local contexts. A different picture emerges for PFOS. In this case, municipal WWTP present the widest range, the highest values and a median level significantly higher than that of atmospheric deposition. From a review of effluent concentrations of a broad spectrum of micropollutants in conventional municipal WWTPs in Europe and USA (Margot et al., 2015), typical levels of $0.012 \mu\text{g l}^{-1}$ and $0.013 \mu\text{g l}^{-1}$ emerged for PFOS and for PFOA, respectively. Median concentrations measured in this study are approximately half of those levels, although peaks up to $0.12 \mu\text{g l}^{-1}$ for PFOS and $0.046 \mu\text{g l}^{-1}$ for PFOA were recorded. As detailed in Appendix C (Table C.17), PFOS concentration in municipal effluents is considerably higher than in industrial effluents. The comparative analysis also revealed significant differences among classes of municipal WWTPs (Table C.18). Discharges from plants larger than 150,000 $\text{PE}_{\text{COD}120}$ contained significantly more Ni, Zn, PFOS and PFOA than the effluents of smaller plants. In this respect, the results of PFOS and PFOA are particularly interesting and relevant, given the currently widespread risk of exceedance of EQS in rivers for PFOS and the potential of point discharges to further deteriorate the situation due to their elevated concentrations. Fig. 8 shows boxplots of the concentrations of these two compounds in the effluents of municipal plants of three different classes and in industrial effluents. Beside the aforementioned differences, this figure illustrates the large variability range of PFOS within large municipal plants and the considerable difference of PFOA levels between the two smaller municipal classes. Given the relatively small available sample size, these results cannot be assumed to statistically represent the entirety of WWTPs in Austria. Nevertheless, they point out interesting relationships, which are worth being further investigated in future research. In conclusion, although the priority should clearly consist of reducing point discharges, this overview across compartments highlights the challenge of achieving major improvements of PFOS in surface waters in the near future. In fact, not only do the results in rivers indicate a widespread exceedance of the established EQS (mean $0.00065 \mu\text{g l}^{-1}$), but such value was even exceeded in several samples of groundwater and bulk deposition.

3.1.5. Concentration levels of PAHs and PFAAs at baseflow and high flow

The rise in total concentration of particulate-bound contaminants with increasing discharge, driven by the higher particulate transport, is a well-known pattern. The relationship between dissolved concentrations and discharge, however, is more complicated. In rivers with substantial input of pollutants through WWTP effluents, concentrations are assumed to be highest at baseflow and to diminish with increasing flow, owing to the dilution effect exerted by the additional volume of less contaminated rainwater. In case of WWTPs not being a significant emission pathway, instead, rainfall events can provoke an increase in dissolved concentrations driven by the input of contaminants through surface runoff, interflow or tile drainages. Fig. 9 presents mean concentrations of PAHs and PFAAs at baseflow and high flow for different types of catchments. Dornbirnerach, Raba and Wulka represent rivers with substantial contribution of WWTP effluents. Results for PFOS and PFOA are in the majority of cases in accordance with the expected dilution effect. However, a notable exception is the much higher concentration of PFOS at high flow in the Wulka river, i.e. in the catchment with the highest contribution of municipal WWTP discharges. PFOS was non-detectable in soils in this catchment, whereas it was found at measurable levels both in atmospheric deposition and in SPM. These results might point to the mobilisation and release of contaminants from the particulate phase, but also to the direct contribution of atmospheric deposition during storm events, which might offset the expected dilution effect. Moreover, all three catchments present higher concentrations of dissolved PAHs at high flow. Also in this case, atmospheric deposition might play an important role, since these compounds show similar or higher median concentration levels in bulk deposition than in rivers (Fig. 3). In this case, however, such pattern might also stem from the mobilisation and shift into the dissolved phase of particulate-bound compounds during their transfer from soil to water. In the other examined catchments, in which WWTP discharge is absent or minimal, concentrations of dissolved PAHs are almost always higher at high flow. As mentioned before, this might be explained through different emission pathways correlated with high flow conditions, such as bulk deposition, surface runoff, interflow and tile drainages. In order to better understand the complex patterns observed for concentrations, it would be necessary to model and quantify emission loads via different pathways.

3.2. Metals

3.2.1. Mercury

With very few exceptions, Hg was consistently detectable in all examined compartments (Table 7 and Fig. 10). This highlights the crucial importance of employing best available analytical methods, since Hg currently results systematically non-detectable in the Austrian national routine monitoring of water bodies (Umweltbundesamt, 2018a). Median values in the dissolved phase of rivers and in

Table 6
PFAs concentration levels in environmental and engineered compartments.

| | Filtered stream water | | SPM | | Soil | | Bulk deposition | | Groundwater | | Municipal WWTP effluent | | Industrial WWTP effluent | |
|------|--|---------------|---|---------------|--|---------------|--|---------------|--|---------------|--|---------------|--|---------------|
| | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g kg}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) |
| PFOS | 0.0021–<0.0010 (<0.0010–0.011) | na-38 (76) | <0.50–<0.50 (<0.25–1.6) | 8-8 (26) | 1.5–<0.70 (<0.25–10) | 8-5 (18) | 0.0025–0.0022 (<0.0010–0.010) | na-6 (17) | 0.0016–<0.0010 (<0.0010–0.014) | na-93 (126) | 0.015–0.0062 (<0.0010–0.12) | 0-1 (34) | 0.059–0.0013 (<0.0010–0.58) | na-7 (18) |
| PFOA | 0.0015–<0.0010 (<0.0010–0.0064) | na-42 (76) | <0.25–<0.25 (<0.25–1.3) | 20-4 (26) | <0.70–<0.70 (<0.25–2.2) | 8-1 (18) | 0.0051–0.0028 (<0.0010–0.016) | na-8 (17) | 0.0014–<0.0010 (<0.0010–0.011) | na-93 (126) | 0.0067–0.0053 (0.0011–0.046) | 0-0 (34) | 0.0070–0.0027 (<0.0010–0.039) | na-4 (18) |

Note: Measured values (in case of minimum or maximum) and calculated values (in case of mean and median) below LOD or below LOQ, are indicated as smaller than the respective specific analytical limits.

groundwater bodies are similar and equal to 0.0047 and 0.0062 $\mu\text{g l}^{-1}$, respectively. Similarly, bulk deposition and municipal WWTP effluents present comparable ranges, with a median concentration of approximately 0.015 $\mu\text{g l}^{-1}$ in both compartments. The median level in municipal WWTP effluents matches very well with the value of 0.016 reported by Margot et al. (2015) for conventional European and North American WWTPs. In the same order of magnitude is also the range identified for industrial WWTP effluents, although these present a lower median of 0.010 $\mu\text{g l}^{-1}$. Values in SPM range from n.q. (<10 $\mu\text{g kg}^{-1}\text{dw}$) to 220 $\mu\text{g kg}^{-1}\text{dw}$, with median 73 $\mu\text{g kg}^{-1}\text{dw}$. Converted into concentrations in water at mean concentrations of particulate matter transport, they are very similar to those measured in the dissolved phase, although during storm events markedly higher values are expected to occur. In soils, Hg is present in a wide range of concentrations, ranging from 10 to 530 $\mu\text{g kg}^{-1}\text{dw}$. Highest values were recorded in forest soils, whereas levels in arable soils were below 60 $\mu\text{g kg}^{-1}\text{dw}$ and in grassland soils they did not exceed 130 $\mu\text{g kg}^{-1}\text{dw}$. Compared to Hg concentrations in topsoil reported for Europe by Lado et al. (2008), these values fall within the lower range.

3.2.2. Cadmium

Similarly to Hg, Cd was mostly detectable in all examined compartments, with exception for municipal WWTP effluents (Table 7 and Fig. 10). Here, it was below 0.020 $\mu\text{g l}^{-1}$ in 70% of the samples and below 0.050 $\mu\text{g l}^{-1}$ in the rest. In a previous survey of Austrian WWTPs conducted by Clara et al. (2012), Cd also resulted systematically either non-detectable or non-quantifiable. Margot et al. (2015) did not mention the frequency of occurrence of Cd in typical WWTPs, but reported a relatively low average concentration of 0.050 $\mu\text{g l}^{-1}$. On the contrary, industrial WWTP effluents represent in case of Cd a potentially relevant, though highly variable, emission pathway. Their level differs largely among industrial sectors, considering the relatively broad range between n.q. (<0.0010 $\mu\text{g l}^{-1}$) and 4.5 $\mu\text{g l}^{-1}$. Atmospheric deposition also represents a potentially relevant pathway. It contains Cd in a relatively narrow range around a median of 0.035 $\mu\text{g l}^{-1}$, which is significantly higher than the level found both in groundwater and in the dissolved phase in rivers. Differently from Hg, particulate concentrations of Cd were considerably higher than dissolved ones and extended over a larger range, even at average conditions of particulate matter concentration. This indicates the dominance of particulate over dissolved transport. As far as Cd content in soil is concerned, the results reveal a pattern similar to that of Hg. Highest values up to 790 $\mu\text{g kg}^{-1}\text{dw}$ were recorded in forest soils. The lowest range (<390 $\mu\text{g kg}^{-1}\text{dw}$) was measured in arable soils, whereas grassland soils present intermediate levels. Related to levels of Cd in European topsoils (Lado et al., 2008), the results of this study are situated between low and intermediate ranges.

3.2.3. Copper

Results for Cu are reported in Table 7 and depicted in Fig. 10. The comparison between different transport ways in rivers shows that in average dissolved transport and particulate transport are equally important, although during storm events much higher values in the particulate phase are expected. Whereas in the dissolved phase of rivers Cu was always measurable, with a median value of 4.4 $\mu\text{g l}^{-1}$, in 60% of groundwater samples it was below the LOQ, namely 0.50 $\mu\text{g l}^{-1}$. Nevertheless, also much higher values up to 603 $\mu\text{g l}^{-1}$ were recorded in groundwater. With respect to emission pathways, it can be observed that atmospheric deposition (median 8.2 $\mu\text{g l}^{-1}$) contains a significantly higher Cu level than municipal WWTP effluents (median 4.4 $\mu\text{g l}^{-1}$). There, Cu was nevertheless always measurable with a range between 1.2 and 9.5 $\mu\text{g l}^{-1}$, which is quite in accordance with the median of 4.3 $\mu\text{g l}^{-1}$ reported by Clara et al. (2012) and the average of 8.3 $\mu\text{g l}^{-1}$ published by Margot et al. (2015). Like in the case of Cd, industrial WWTP effluents have higher though largely heterogeneous concentration levels, given that results vary from 1.7 to 260 $\mu\text{g l}^{-1}$. With respect

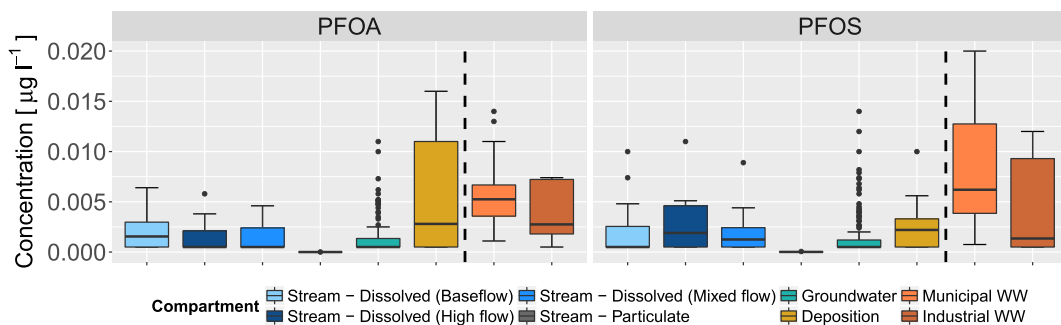


Fig.7. Concentration of PFAAs in environmental and engineered compartments. Lower and upper hinges correspond to first and third quartiles. Values beyond the range of 1.5*IQR are plotted individually. The bar “Stream - Dissolved (Mixed flows)” relates to large rivers and river Zaya, for which composite samples collected at different flow conditions were analysed. Values for the stream particulate phase are estimations derived from concentrations in SPM and related to mean SPM transport. Sample size varies considerably between compartments (see Table 6). To make the graph more readable, extreme outlying values measured in WWTP effluents are not depicted.

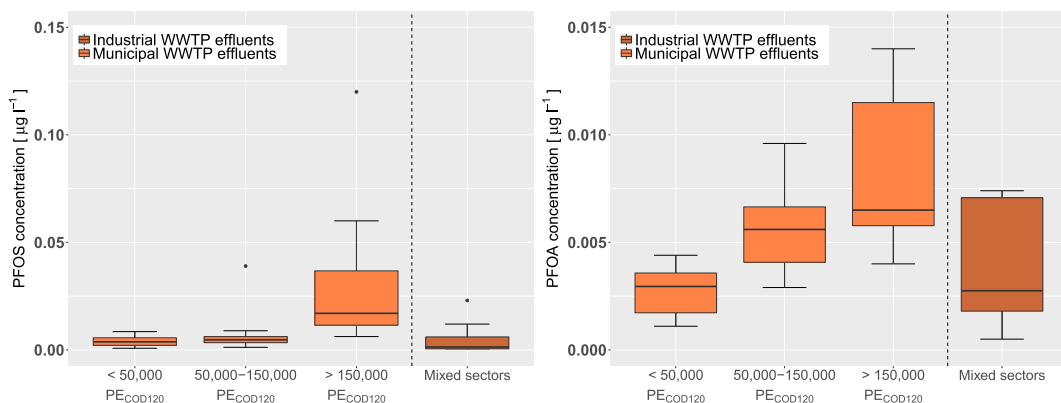


Fig.8. Concentration of PFAAs in effluents of municipal and industrial WWTPs. Lower and upper hinges correspond to first and third quartiles. Values beyond the range of 1.5* IQR are plotted individually. To make the graph more readable, extreme outlying values are not depicted.

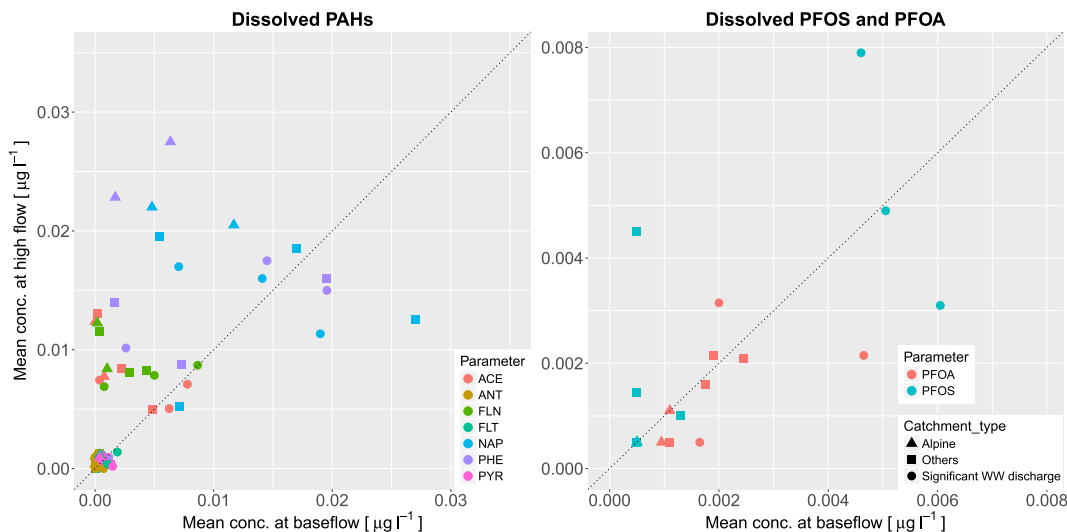


Fig.9. Relationship between dissolved concentration of PAHs and PFAAs in stream water at baseflow and high flow conditions. PAH compounds systematically n.d. or n.q. are not shown.

to soils, no distinct differences were detected among land uses, with all of them extending more or less broadly over the range 13,000–34,000 $\mu\text{g kg}^{-1}\text{dw}$. Such levels correspond to the relatively low up to intermediate ranges of Cu content in topsoil recently identified by Ballabio et al. (2018) across whole Europe.

3.2.4. Nickel

The occurrence of Ni in most compartments is similar to that of Cu,

although concentration ranges differ considerably (Table 7 and Fig. 10). In contrast to Cu, the dominance of particulate transport for Ni is manifest even at average flow conditions. In the dissolved phase, concentrations for most rivers range between 0.37 and 3.7 $\mu\text{g l}^{-1}$, but values between 5.2 and 9.4 $\mu\text{g l}^{-1}$ were recorded in the river Ötztaler Ache. Given that this is predominantly fed by a glacier, these results might point to a higher geogenic background. Results for groundwater are quite similar, with Ni being measurable in almost all samples and

Table 7
Heavy metals concentration levels in environmental and engineered compartments.

| | Filtered stream water | | SPM | | Soil | | Bulk deposition | | Groundwater | | Municipal WWTP effluent | | Industrial WWTP effluent | |
|----|--|---------------|---|---------------|---|---------------|--|---------------|--|----------------|--|---------------|--|---------------|
| | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g kg}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g kg}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) | Mean-Median (Min-Max) [$\mu\text{g l}^{-1}$] | n.d.-n.q. (n) |
| Hg | 0.0079–0.0047 (0.00073–0.089) | na-0 (42) | 74-73 (<10–220) | 0-0 (26) | 129-75 (10–530) | 0-0 (18) | 0.017–0.016 (0.0062–0.033) | na-0 (17) | 0.014–0.0062 (<0.00050–0.096) | 1-7 (128) | 0.019–0.015 (0.0055–0.067) | 0-0 (35) | 0.017–0.010 (0.0035–0.048) | na-0 (18) |
| Cd | 0.011–0.0070 (<0.0010–0.067) | na-6 (43) | 400–390 (170–720) | 0-0 (26) | 400–340 (190–790) | 0-0 (18) | 0.039–0.035 (0.020–0.090) | na-0 (7) | 0.029–0.010 (<0.0025–0.37) | 10–11 (62) | <0.020–<0.020 (<0.020–<0.050) | 23–9 (32) | 0.65–0.062 (<0.0010–4.5) | na-1 (18) |
| Pb | 0.17–0.11 (<0.010–1.7) | na-4 (36) | 18,000–18,000 (4000–35,000) | 0-0 (26) | 28,000–24,000 (16,000–53,000) | 0-0 (18) | 1.5–1.4 (0.4–3.9) | na-0 (7) | 0.20–0.12 (0.036–1.0) | 0-0 (60) | <0.50–<0.50 (<0.10–<0.50) | 10–22 (32) | 1.6–0.65 (<0.010–8.5) | na-1 (18) |
| Ni | 1.9–1.1 (0.37–9.4) | na-0 (36) | 36,000–30,000 (21,000–64,000) | 0-0 (26) | 29,000–28,000 (15,000–55,000) | 0-0 (18) | 3.9–1.0 (0.35–22) | na-0 (7) | 0.73–0.45 (<0.050–9.4) | 0-2 (56) | 7.6–5.4 (<1.0–30) | 1–15 (36) | 52–1.4 (0.19–290) | na-0 (18) |
| Cu | 5.2–4.4 (0.79–19) | na-0 (36) | 33,000–31,000 (19,000–57,000) | 0-0 (26) | 23,000–21,000 (13,000–34,000) | 0-0 (18) | 8.4–8.2 (3.8–14) | na-0 (7) | 3.4–<0.50 (<0.050–603) | 703–580 (2143) | 4.7–4.4 (1.2–9.5) | 0-0 (36) | 50–5.5 (1.7–260) | na-0 (18) |
| Zn | 6.8–5.8 (1.1–29) | na-0 (36) | 130,000–130,000 (55,000–240,000) | 0-0 (26) | 85,000–81,000 (63,000–120,000) | 0-0 (18) | 63–46 (34–130) | na-0 (7) | 56–9.2 (<0.50–3560) | 275–287 (2143) | 23–20 (7.3–47) | 0-0 (35) | 61–16 (3.8–330) | na-0 (18) |

Note: Measured values (in case of minimum or maximum) and calculated values (in case of mean and median) below LOD or below LOQ, are indicated as smaller than the respective specific analytical limits. Note 2: the ANIP network partially relies on nickel alloy containers. Therefore, the analysis of Cd, Cu, Ni, Pb, and Zn in part of the samples was discarded.

showing median and maximum concentrations of 0.45 and 9.4 $\mu\text{g l}^{-1}$, respectively. Unlike all other metals examined in this study, concentrations of Ni in atmospheric deposition were not higher than those measured in rivers. In contrast to the almost negligible role of atmospheric deposition, WWTP discharges present substantially higher Ni levels. In municipal WWTP effluents, Ni was measurable in approximately half of the samples, with a median of 5.4 $\mu\text{g l}^{-1}$. This corresponds quite well with the median of 4.1 $\mu\text{g l}^{-1}$ reported by Clara et al. (2012) and the average of 4.9 $\mu\text{g l}^{-1}$ published by Margot et al. (2015). Industrial WWTP effluents present an even broader range, extending from 0.19 to 290 $\mu\text{g l}^{-1}$. As far as soils are concerned, both lowest (15,000 $\mu\text{g kg}^{-1}\text{dw}$) and highest (55,000 $\mu\text{g kg}^{-1}\text{dw}$) values were measured in background forest soils. Arable soils present a narrower range between 19,000 and 32,000 $\mu\text{g kg}^{-1}\text{dw}$, which correspond to intermediate up to high levels found in European topsoils (Lado et al., 2008).

3.2.5. Lead

Pb was present at measurable concentration levels in almost all river and groundwater samples (Table 7 and Fig. 10), with median levels of 0.11 $\mu\text{g l}^{-1}$ and of 18,000 $\mu\text{g kg}^{-1}\text{dw}$ in the dissolved phase of rivers and in SPM, respectively, and with a median of 0.12 $\mu\text{g l}^{-1}$ in groundwater. Particulate transport appears to be largely dominant even at average flow conditions. Among the considered emission pathways, atmospheric deposition and industrial WWTP effluents reveal similar ranges, with median values of 1.4 $\mu\text{g l}^{-1}$ and 0.65 $\mu\text{g l}^{-1}$, respectively. As for municipal WWTP effluents, Pb was systematically below the LOD or the LOQ. The resulting mean below < 0.50 $\mu\text{g l}^{-1}$ is lower than the average value of 0.80 $\mu\text{g l}^{-1}$ published by Margot et al. (2015). In soils, Pb shows a pattern similar to that of Hg and Cd, with highest levels measured in background forest areas (19,000–53,000 $\mu\text{g kg}^{-1}\text{dw}$) and lowest values recorded in arable soils (16,000–23,000 $\mu\text{g kg}^{-1}\text{dw}$). These correspond to the relatively lower range reported by Lado et al. (2008) for topsoils across Europe.

3.2.6. Zinc

Results for Zn are presented in Table 7 and in Fig. 10. In the dissolved phase in rivers, Zn is present at concentrations similar to those of Cu, with a median of 5.8 $\mu\text{g l}^{-1}$. Both SPM and soils, however, contain much higher levels of Zn than of all other examined metals, with medians of 130,000 and 81,000 $\mu\text{g kg}^{-1}\text{dw}$, respectively. With peak values of 120,000 $\mu\text{g kg}^{-1}\text{dw}$, Zn is the only examined metal to show highest levels in soils with grassland use. With a median of 73,000 $\mu\text{g kg}^{-1}\text{dw}$ and a maximum of 85,000 $\mu\text{g kg}^{-1}\text{dw}$, arable soils fall within the lower limit of the range found in European topsoils (Lado et al., 2008). In groundwater, Zn presents a median of 9.2 $\mu\text{g l}^{-1}$ and an extremely variable range extending up to 3560 $\mu\text{g l}^{-1}$, which highlights the strong differences of background geological concentrations. Among atmospheric deposition and WWTP effluents, the first emerges as comparatively high, with a median value of 46 $\mu\text{g l}^{-1}$. In municipal WWTP effluents, the median of 20 $\mu\text{g l}^{-1}$ found in this study is lower than the median of 31 $\mu\text{g l}^{-1}$ identified by Clara et al. (2012) and than the average of 31 $\mu\text{g l}^{-1}$ published by Margot et al. (2015). As already observed for other metals, industrial WWTP effluents show for Zn a much broader range of concentrations, extending from 3.8 $\mu\text{g l}^{-1}$ up to 330 $\mu\text{g l}^{-1}$.

3.2.7. Concentration levels of metals at baseflow and high flow

Similarly to what was previously observed for PAHs and PFOS (Fig. 9), dissolved concentrations of metals present partially counter-intuitive patterns in their relationship to river discharge. Within the three study catchments with significant WWTP effluent contribution (Dornbirnerach, Raba and Wulka), higher concentrations of metals in the dissolved phase were recorded at higher river flow (Fig. 11). Hypothesizing a dilution effect by the input of less contaminated rainwater into the river, lower concentrations of dissolved metals could have been

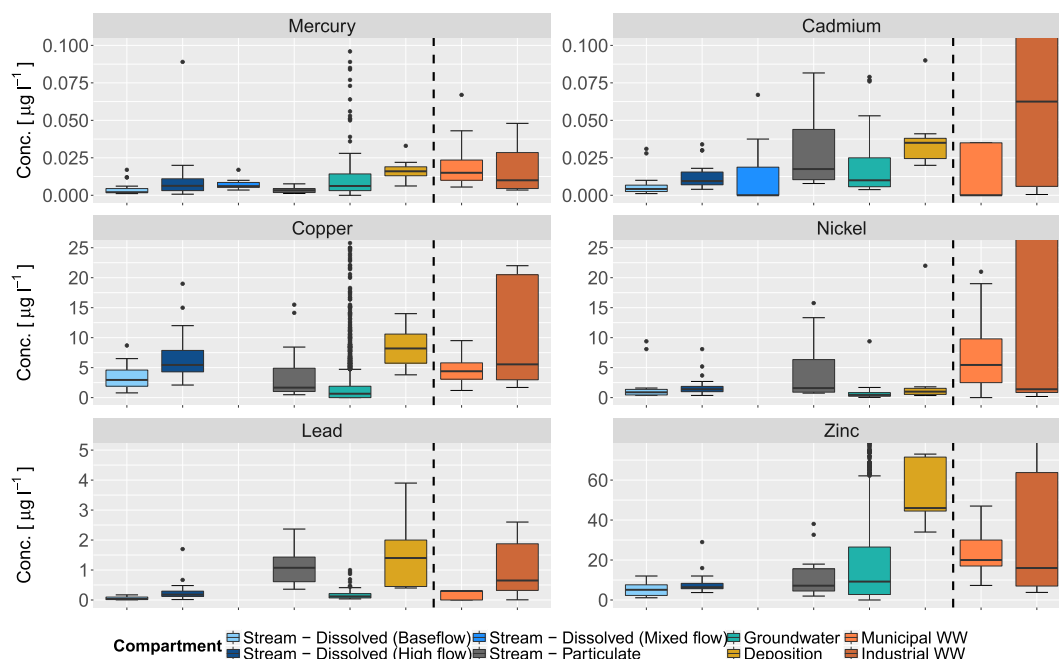


Fig. 10. Concentration of metals in environmental and engineered compartments. Lower and upper hinges correspond to first and third quartiles. Values beyond the range of $1.5 \times \text{IQR}$ are plotted individually. The bar “Stream - Dissolved (Mixed flows)” relates to large rivers and river Zaya, for which composite samples collected at different flow conditions were analysed. Values for the stream particulate phase are estimations derived from concentrations in SPM and related to mean SPM transport. Sample size varies considerably between compartments (see Table 7). To make the graph more readable, extreme outlying values measured in bulk deposition, groundwater and WWTP effluents are not depicted.

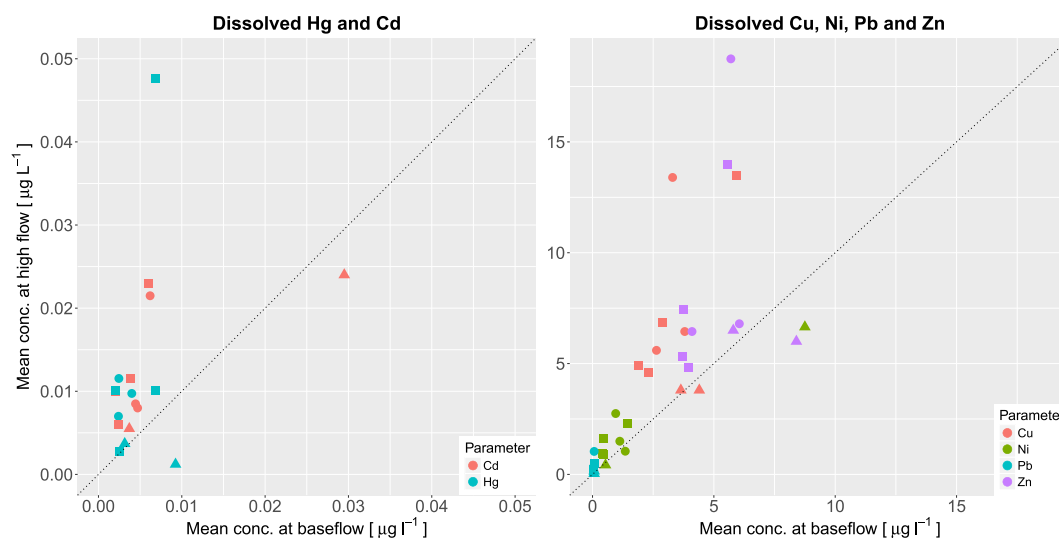


Fig. 11. Relationship between dissolved concentration of metals in stream water at baseflow and high flow conditions.

assumed instead. Atmospheric deposition might indirectly (through surface runoff, interflow and tile drainages) be responsible for this incongruity, since metals present similar or higher median concentration levels in bulk deposition than in rivers (Fig. 10). Nevertheless, such pattern might also stem from the mobilisation and shift into the dissolved phase of particulate-bound compounds during their transfer from soil to water. Interestingly, in the background mountain rivers without any relevant WWTP effluent contribution (Ötztaler Ache and Reichramingbach), whereas dissolved PAHs show higher concentration levels at higher flows, most metals diminish their concentrations with increasing flow.

4. Conclusions and outlook

Occurrence and concentration levels of a broad spectrum of micropollutants were investigated in a number of environmental and engineered compartments in Austrian river catchments. The parallel analysis of different compartments sheds light on the potential relevance of different transport and emission pathways for specific compounds. For examples, it was observed that some contaminants, such as selected PAHs and butyltin compounds, are present at substantially higher levels in rivers and groundwater than in municipal and sometimes even industrial WWTP effluents. It was shown and quantified that atmospheric deposition and WWTP discharges have alternately highest concentration levels for different compounds, even within the same group of contaminants. For example, atmospheric

deposition presents the broadest range and the highest values for PFOA, whereas the highest range was observed for PFOS in municipal WWTP effluents. Significantly higher concentration levels in atmospheric deposition than in municipal WWTP effluents were also observed for most metals, namely Cd, Cu, Pb and Zn, whereas the opposite was true for Ni. Further, it was striking to observe for PFOS that, despite municipal WWTP effluents presenting highest pollution levels, concentrations not only in rivers but also in deposition and groundwater sometimes exceed the EQS set for surface water bodies. Although soil erosion could not be explicitly quantified and compared to other emission pathways within this study, an overview of the occurrence and of the levels of contaminants in soils of different land uses and in suspended particulate matter was presented and discussed. This generally indicates whether a potential contamination of water bodies through erosion exists and, if so, to which extent. Very low or null concentration levels in soils and in SPM suggest that soil erosion is not a relevant emission pathway for PFAAs, organotin compounds and low molecular weight PAHs, whereas the findings point to a potentially relevant, although variable, contribution for the other examined compounds. Moreover, the study revealed some patterns which are either counterintuitive or difficult to explain with current knowledge. One example consists of higher levels of contaminants in the dissolved phase at higher flow conditions in rivers with substantial WWTP discharges, which contradicts the assumption of predominant dilution effects. Such pattern might result from the mobilisation of pollutants from soil or suspended particulate matter into the dissolved phase. Alternatively, it could indicate that contaminants are transported through polluted atmospheric deposition, which presents higher concentration levels than WWTP effluents for numerous compounds, and then enter water bodies through surface runoff during storms events. These hypotheses require however being tested with further targeted research. Although such analysis was beyond the scope of this manuscript, the unique dataset generated in this work may be employed to explore more in detail: 1) regional differences and 2) relationships between occurrence and levels of specific compounds and relevance of specific emission pathways with land use and other catchment properties. Further, a relevant line of future research would be to move beyond the analysis of concentrations, by linking these results with water runoff components and suspended solids transport, in order to model both emission and river loads. This would enable to quantify the actual relevance of different transport and emission pathways at sub-catchment level.

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Appendix ASupplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2018.10.074>.

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