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Development and testing of an efficient micropollutant monitoring strategy across a large watershed

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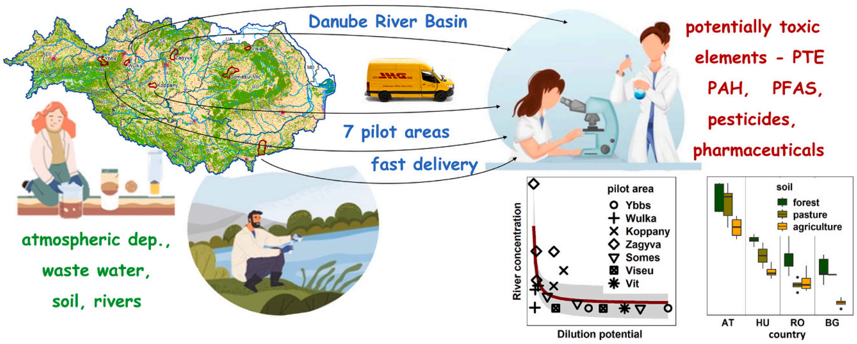
HIGHLIGHTS

- 44 micropollutants monitored in 7 medium-sized sub-catchments of the Danube River Basin
- All major groups of micropollutants and most important pathways sampled with a smart approach
- Developed method capable of deriving patterns over large heterogeneous areas
- Pollutants dependent on economic development and/or geogenic characteristics identified
- Practice of applying uniform emission factors needs reconsideration

GRAPHICAL ABSTRACT



Abbreviations: AD, atmospheric deposition (samples); CAS, chemical abstracts service; DM, dry matter; DRB, Danube River Basin; HS, hazardous substances; ICPDR, International Commission for Protection of the Danube River; LOD, limit of detection; logK_{ow}, logarithm of the octanol-water partitioning coefficient (to reflect hydrophobicity); logK_{oc}, logarithm of the organic carbon partitioning coefficient (to reflect affinity to adsorb to organic particles); LOQ, limit of quantification/quantitation; PAH, polycyclic aromatic hydrocarbons; PA, pilot area(s); PFAS, per- and poly-fluoroalkyl substances; PTE, potentially toxic elements; WW, wastewater (samples); WWTP, wastewater treatment plant(s).

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ABSTRACT

In recent decades, extensive monitoring programmes have been conducted at the national, international, and project levels with the objective of expanding our understanding of the contamination of surface waters with micropollutants, which are often referred to as hazardous substances (HS). It has been demonstrated that HS enter surface waters via a number of pathways, including groundwater, atmospheric deposition, soil erosion, and urban systems. Given the ever-growing list of substances and the high resource demand associated with laboratory analysis, it is common practice to quantify the listed pathways based on emission factors derived from temporally and spatially constrained monitoring programmes. The derivation calculations are subject to high uncertainties, and substantial knowledge gaps remain regarding the relative importance of the unique pathways, territories, and periods.

This publication presents a monitoring method designed to quantify the unique emission pathways of HS in large geographical areas characterized by differences in land use, population, and economic development. The method will be tested for a wide range of HS (ubiquitous organic and inorganic pollutants, pesticides, pharmaceuticals) throughout small sub-catchments located on tributaries. The results of the test application demonstrate a high diversity of both emission loads and instream concentrations throughout different regions for numerous substances. Riverine concentrations are found to be highly dependent on the flow status. Soil concentration levels of polycyclic aromatic hydrocarbons (PAH) and perfluoroalkyl substances (PFAS) are found to be in proportion, whereas that of potentially toxic elements (PTE) in a reverse relationship with economic development. In many instances, concentration levels are also contingent upon land use.

The findings of this study reinforce the necessity for the implementation of harmonised and concerted HS monitoring programmes, which should encompass a diverse range of substances, emission sources, pathways and geographical areas. This is essential for the reliable development of emission factors.

1. Introduction

There is a growing awareness of the fact that a substantial portion of the chemical substances produced to support everyday life have adverse side effects when entering the environment – even if the concentrations are in the order of magnitude of μg l^{-1} or below (EEA, 2018; Persson et al., 2022). The Stockholm Convention (SC, 2009), the Environmental Quality Standards Directive (EC, 2008), and the EU Green Deal's Zero Pollution Action Plan (EU, 2022) represent a few of the milestones on the path towards the registration, quantification, and mitigation of environmental pollution, particularly that of aquatic ecosystems, caused by hazardous substances (HS). The guidance document on the implementation of the Environmental Quality Standards Directive (WFD-CIS, 2018, 2011) prescribes the inventorying of emissions, discharges, and losses of HS. It requires substantial efforts regarding sampling and laboratory analysis (i.e., monitoring) (Sousa et al., 2018; van Gils et al., 2020; WFD-CIS, 2012).

Most recently, the EU has proposed a recast of the Urban Wastewater Treatment Directive, which would require quaternary treatment at wastewater treatment plants (WWTP) with a capacity between 10,000 and 100,000 population equivalents if situated on areas at risk of exceedance of the standards for priority substances. In the event that risks have been identified, thresholds more stringent than those indicated in the annex of the directive have to be applied (EC, 2022a). The identification of areas at risk may prove challenging due to the considerable spatial heterogeneity in the usage and emission of Hs across countries (Fabre et al., 2023; Schwarzenbach et al., 2006). The simultaneously published proposal amending three water-related directives (the Water Framework Directive, the Groundwater Directive, and the Directive on Environmental Quality Standards) (EC, 2022b) adds a range of crucial water pollutants including PFAS, pharmaceuticals, and pesticides to the list of priority substances for surface water (Backhaus, 2023). In addition to the increasingly stringent policies, there is a significant lack of knowledge regarding the fate of HS in the environment (Seller et al., 2023; Wang et al., 2020) (Schmidt, 2018).

The primary means of addressing knowledge gaps is through the implementation of measurement campaigns. In order to design an effective measurement programme, it is essential to have a clear understanding of the levels of pollution and the behavior of pollutants. It is also crucial to consider spatial and temporal patterns, such as pollution hotspots and the occurrence of continuous versus seasonal emissions. This allows for the development of a monitoring programme that is tailored to the specific needs of the area in question. Designing a monitoring programme is therefore a recursive process, with preliminary modeling often forming a fundamental step in this process. Conversely, modeling is of great importance for extrapolating limited monitoring data to large geographic areas. However, when upscaling models to larger areas, the "curse of geography" arises: the larger the area covered by a model, the less it will be able to accurately represent small-scale processes and patterns, either due to a lack of data or computational capacity (Moser et al., 2018). Even when applying GIS methods, in-detail modeling of larger areas might run into computing capacity problems. Models are generally fed with emission factors derived either (1) from monitoring programs (monitoring program) that are constrained spatially and temporally and/or regarding the substances; or (2) by merging data from various sources overseeing thereby differences in monitoring methods and spatiotemporal validity of the unique monitoring program. Spatial and temporal differences are seldom accounted for (Chaves et al., 2020; Zhao et al., 2021). Furthermore, in case of models covering large areas, other types of input data are in general heterogeneous both in terms quantity and quality. This is of particular importance in the context of data-driven approaches applied to emission models (Fuchs et al., 2017; Jolánkai et al., 2020; Kittlaus et al., 2022) (van Gils et al., 2019).

There is an emerging need to further identify spatial and temporal patterns, and causal relationships describing the behavior of HS. This can be achieved through the implementation of a harmonised and concerted, yet holistic monitoring programme that encompasses the wide spectrum of geographical, hydrological, societal and economic characteristics of the region in question. Due to the low concentration levels, the long (and ever-growing) list of substances, and the special equipment and personnel needs, the determination of the concentration of HS is costly. Therefore, monitoring programmes must be effective and efficient. Effective monitoring should cover the diverse pathways as well as the widest possible groups of pollutants. It should be noted that the most efficient use of laboratory resources is achieved when the minimum number of samples is delivered to the laboratory, provided that this still allows the specific purpose to be accomplished (Gavrilescu et al., 2015). At the same time, it should be possible to deliver figures allowing for the quantification of representative mass flows (loads) (Sousa et al., 2018; van Gils et al., 2020).

The process of designing a monitoring programme encompasses a number of key stages, including the delineation of the area to be monitored, the determination of the exact sampling spots and times, and the determination of the measurement equipment. It also includes the fixing of the transportation and sampling delivery methods, as well as the data checking, storage, and accessibility issues (Chapman et al., 2016; WFD-CIS, 2009) (UNEP, 2011). In general, sampling devices range from the simplest grab sampling devices (e.g. sampling rod) to the most costly autosamplers, which are operated by measuring the quantity and/or quality of the water in real-time. These devices can be passive or active. Stratified sampling is generally used to focus the sampling on one or more aspects of the sampled media; strata can be created randomly or intentionally. Composite samples are created to aggregate information over samples. This can be done before or after the measurements have been taken. In the former case, the main goal is typically to reduce the number of measurements and associated costs. In the latter case, the aim is to simplify the information. One of the key aspects of designing a monitoring programme is to select the compounds to be determined from the samples. Given the multitude of compounds that can be analysed, this is especially challenging for HS. These compounds can be classified according to various criteria, including their origin (natural versus anthropogenic), occurrence (ubiquitous versus scarce/specifically occurring), basic chemical properties (inorganic versus organic), and area of application (industrial chemicals, pharmaceuticals and personal care products, pesticides).

The Danube Hazard m^{3}c was an InterReg project (long title: “Tackling hazardous substances pollution in the Danube River Basin by Measuring, Modeling-based Management and Capacity building”) launched in the Danube Transnational Program aiming to reduce HS water pollution by understanding of the status quo and improving knowledge. In particular, project tasks were (1) integrating and harmonizing available existing data of HS concentrations (2) designing and implementing a monitoring program aiming to fill the gaps identified during building up a database on HS concentrations; (3) setting up HS emission models both at PA and the DRB level, running various management scenarios with them; and (4) activities aiming at fostering institutional capacity building in the DRB countries (DTP, 2023).

1.1. Objectives of the present study

The objective of this study is to present the design, implementation, and utility of a monitoring program that was developed as part of the Danube Hazard m^{3}c project (Zoboli et al., 2023). The monitoring program aimed to gather information pertinent to a significant portion of the Danube River Basin (DRB), the most prevalent pathways of pollution, and HS affecting the most crucial groups with regard to application and environmental behavior. To this end, data were collected from selected pilot areas (PA) situated in disparate regions of the DRB. In order to achieve this objective, all pilot areas (PAs) and sampling points were situated on tributaries of the Danube rather than on the main river. Consequently, the current work does not provide data on the contamination of the Danube River. The goal was to generate information on the occurrence and concentration of hazardous substances (HSs) in river water, atmospheric deposition, municipal and industrial emitters, and soils. The ultimate goal of the implemented programme was twofold: (a) To support the establishment of an inventory of HS concentrations in emission pathways and surface water bodies (Kittlaus et al., 2024) as well as (b) to support the modeling of HS emission both at the pilot catchment (Broer et al., 2023; Gabriel et al., 2023, 2022) and the DRB scale (Kovacs et al., 2023b, 2023a).

Given the high resource demand for sampling and lab analysis of HS concentrations, the monitoring program aimed to collect the maximum information possible with the given, relatively constrained monitoring resources while generating information relevant for large areas of the DRB. To draw sound comparisons, a novel approach was employed, whereby the same pathway-overarching monitoring concept was applied simultaneously to different catchments in different countries. The potential for reducing the number of samples and, consequently, the associated costs for chemical analyses by applying a concept based on composite samples will be discussed. The latest statistical methods will be employed to select sampling locations, with sample collection, where feasible, conducted using modern equipment. To assess their representativeness, the results and newly developed relationships will be compared to those described in the literature. It is anticipated that the simultaneous application of the same harmonised concept to different types of catchments in countries with very different hydrogeological and socioeconomic characteristics will enable the investigation of the variability of these relationships and ratios, and – where necessary – their reassessment. Conclusions will be drawn regarding the appropriateness and limitations of the approach of large-scale emission modeling based on the extrapolation of emission factors.

2. Methods

To obtain results capable of establishing relationships that are valid for a wide range of HS over a large area of the DRB, while at the same time remaining within reasonable resource constraints, both the list of the analysed substances and the areas of monitoring had to be restricted. In the following section, we will describe the considerations that informed our selection of a countable number of substances, the pilot areas and the pathways to be monitored. This was done to generate highly relevant information while keeping the number of substances and samples at the lowest possible level. This was accomplished in four steps: (1) The selection of substances to be monitored, along with the corresponding laboratory methods. (2) The selection of pilot areas and sampling locations. (3) The determination of sampling times and frequencies and the creation of composites. (4) The development of an adequate data management protocol.

2.1. Selection of substances to be analysed

Legal monitoring obligations and results of previous projects played a major role in the selection of the substances to be monitored, i.e. the initial list consisted of substances represented in any of the following regulations: EQS-Directive (EC, 2008; European Parliament & Council, 2013), watch list elements & candidates (Cortes et al., 2020; Loos et al., 2018). In addition, the prioritization of emerging contaminants for the Danube River Basin based on monitoring and modeling within the EU SOLUTIONS project and the Danube River Basin’s River Basin Specific Pollutants (ICPDR, 2015) were used as a basis for the selection. In this way, it was ensured that the selected substances were of wide interest due to their spread occurrence and expected effect on ecosystems in the studied region.

The following aspects were subsequently considered to choose the final list: (a) both organic and inorganic HS should be included; (b) both ubiquitous substances and others with specific occurrence should be included; (c) all the major polluting sectors (such as urban areas, industry, agriculture) should be represented by at least two substances to allow for comparison; (d) selected substances should cover a wide range of chemical properties (in terms of basic chemical characteristics, e.g. hydrophobicity); and (e) practical reasons, like available analytical methods. To optimize the ratio between obtained information and invested resources, the number of substances was limited to selected indicators of groups emitted via different emission pathways.

The selected substances are representatives of either of the following six groups of substances: (a) inorganic substances of both natural and anthropogenic origin (b) organic substances of both natural and anthropogenic origin; (c) per- and polyfluoroalkyl substances (PFAS) originally classified as industrial chemicals but being ubiquitous nowadays; (d) phenols; (e) substances of intensive agricultural use and (f) pharmaceuticals.

Regarding group (a), eight heavy metals & metalloids: Cr, Ni, Cu, Zn, As, Cd, Pb and Hg were investigated; in the case of river water, both total and dissolved forms were measured. The total forms enable establishment of mass balances / budgets whereas the dissolved forms are relevant for estimating effects on the ecosystems. Throughout the paper, we will refer to this group of pollutants as potentially toxic elements (PTE) (Budai and Clement, 2018; Milačič et al., 2019; Singh et al., 2016; Vijayakumaran Nair et al., 2022). Concerning group (b) the 16 PAHs according to the United States Environmental Protection Agency list were determined as representatives of widely used, ubiquitous substances, many of which are carcinogenic. Although this selection of PAH is of historical origin and the mentioned reasons might not justify this selection anymore, we selected them because this is the list of PAH was well established, and comparable data is available (Buzás et al., 2008; Chiffre et al., 2015) (Foan et al., 2012). Regarding PFAS (group (c)), the concentration of 10 carbocyclic +3 sulfonic acids was determined. Regarding group (d), bisphenol A (BPA) and the two alkylphenols octyl- and 4-nonylphenol were investigated being industrial chemicals that have received considerable attention due to high production and widespread usage (Huang et al., 2012). The two pesticides tebuconazole and metolachlor were used as indicators of group (e) (Campanale et al., 2021; Carvalho, 2017; Székács et al., 2015) because they are widely used in the Danube River Basin. Regarding group (f), the concentration of carbamazepine and diclofenac was determined, because both are reported to be useful for tracing sewage-originated contamination of rivers (Luo et al., 2014; Yang et al., 2017). While the first three groups of substances (PTE, PAH, and PFAS) were represented with 8+ substances each, only two+two pesticides and pharmaceuticals were measured. Even if these latter two groups also represent highly concerning and wide classes of contaminants, the constrained resources available for the monitoring program did not allow for a higher number of substances to be measured. See the Appendix for the detailed list of analysed substances, the respective analysis norms, lab methods, LOD, and LOQ values.

2.2. Selection of pilot areas for the implementation of the sampling program

The challenges in monitoring HS particularly pronounced when dealing with a river basin such large and complex (with regards to geographical, economic, and societal indicators and circumstances) as the DRB, covering >800,000 km^2 and extending over the territories of countries in Europe with higher and lower economic strength (ICPDR, 2021; Lindim et al., 2016). The objective of the current project, was not to monitoring HS levels in the Danube itself. Instead, the aim was to further enhance our understanding of the origin and spreading of substances by implementing monitoring on small tributaries and their catchments.

The following points were taken into account when selecting pilot areas (PA). (a) PA should be located in different Danubian countries and present distinctive traits with respect to climate, hydrology, land-use and pollution pressure. (b) PA should be small enough to allow the investigation of locally relevant/important emission sources and pathways but – at the same time – large enough to be of relevance on national and DRB level. (c) They should be relatively homogeneous (in terms of hydrogeological conditions and anthropogenic activities) or subdividable into such sub-catchments. (d) Smaller PA and sub-catchments (sub-catchment: pilot area sub-catchment[s]) of larger PA should be selected/ delineated so that the pollution in them either (i) be typical for a broader region in the country (no singularities); (ii) show a strong predominance of one emission sector (e.g. municipal, industrial, agricultural) or represent pristine ("background") situations and (iii) be of national relevance. (e) Requirement for pre-existence of HS measurements: an inventory of main municipal and industrial emitters and knowledge about level of HS in environmental media/pathways should (at least partly) be available. (f) Reachability from the project partners (PROJECT PARTNER) location and on-site locations suitable to set up river monitoring sites should underline the appropriateness of a candidate PA.

Considering the above, a total of 7 PA from the DRB (2 from Austria, 2 from Hungary, 2 from Romania and 1 from Bulgaria) were included in the project. In the Ybbs PA (Austria), the headwater sub-catchments "AYH" and "AYU" represent alpine vs. lowland conditions, respectively: "AYH" is characterized by significantly lower yearly mean temperature, higher rainfall and specific runoff and lower population density. The Urlbach tributary of the Ybbs (sampled at station "AYU") is characterized by an agricultural catchment. Station "AYL" is the PA outlet point. In the Wulka PA (Austria), all three sub-catchments are dominated by agricultural land use but they significantly differ in the point sources influence: the Eisbach (sampled at station "AWE") receives high amount of WW effluent while the Nodbach (sampled at "AWN") has no WW effluent. In the headwater catchment of the Koppany PA, Hungary ("HKH") the special situation of relatively high fraction of WW is combined with relatively low population density due to a wastewater diversion/redirection. "HKT" is the PA outlet point. The whole Koppany PA is highly erosive due to the soil condition and the large-field arable land cultivation applied in the region. In the Zagyva PA (Hungary), the headwater sub-catchments "HZN", "HZT" and "HZH" are characterized by very similar sizes, geological and socio-economical conditions and only differ in the dominant land use type: they are dominated by forest, urban and agricultural land uses, respectively. "HZT" has high WW fraction. "HZ6" is the PA outlet point cumulating the above effects. In the Somes PA, Romania, the two headwater sub-catchments "RSU" and "RNR" are relatively pristine: low number of inhabitants, dominance of forests and arable land in the former and the latter, respectively. The lowest part ("RSD") has high population density and relatively high fraction of WW. Pollution in the Viseu PA (Romania) is determined by inappropriate handling of abandoned mines; the PA is subdivided into two sub-catchment: "RVC" (upper) and "RVV" (lower part). Regarding the Vit PA in Bulgaria, the two upstream headwater sub-catchments "BVB" and "BVC" are both characterized by almost 90 % of forests and natural vegetation, very low population density and almost no or no influence of WW; whereas the lower part ("BVD") is dominated by arable land use, higher population density and some influence of WW (Fig. 1, Table 1). For data on the unique sub-catchment, see Table A2 in the Appendix.

2.3. Sampling program

The design of the sampling programme presented a challenge in that it had to collect the least number of samples that would still allow for the detection of the most important spatial and temporal patterns. In order to ensure that measurement results could be compared across the DRB, a sampling programme as similar as possible was implemented in each PA. In order to ensure that the implementation of monitoring in the different PAs was as similar and harmonised as possible despite different specific constraints, the basic principle was to set the bar as high as possible, such that lowering it to a certain scale would still lead to reliable and comparable results.

In selecting the sampled pathways, the objective was to encompass both major types of pollution, namely point sources and diffuse sources. With regard to the former, both municipal and industrial wastewater treatment plant (WWTP) in- and effluents were sampled, with the addition of mining drainage effluents in the Viseu Protected Area (PA). With respect to the latter, bulk atmospheric deposition and soil samples were collected. In addition to emission sources, river water at the major tributaries and the outflow points of the pilot areas was sampled. Stratification was applied to focus measurements according to certain properties of the sampled media. In the case of AD and WW, strata were intended to distinguish between seasons, with the sampling action repeated seasonally throughout one year. In the case of soil sampling, strata differentiated between land uses and sub-catchments. In the case of river samples, stratification was employed to distinguish between low-flow (river low flow) and high-flow (river high flow) periods.

The creation of composites was intended to minimise the number of

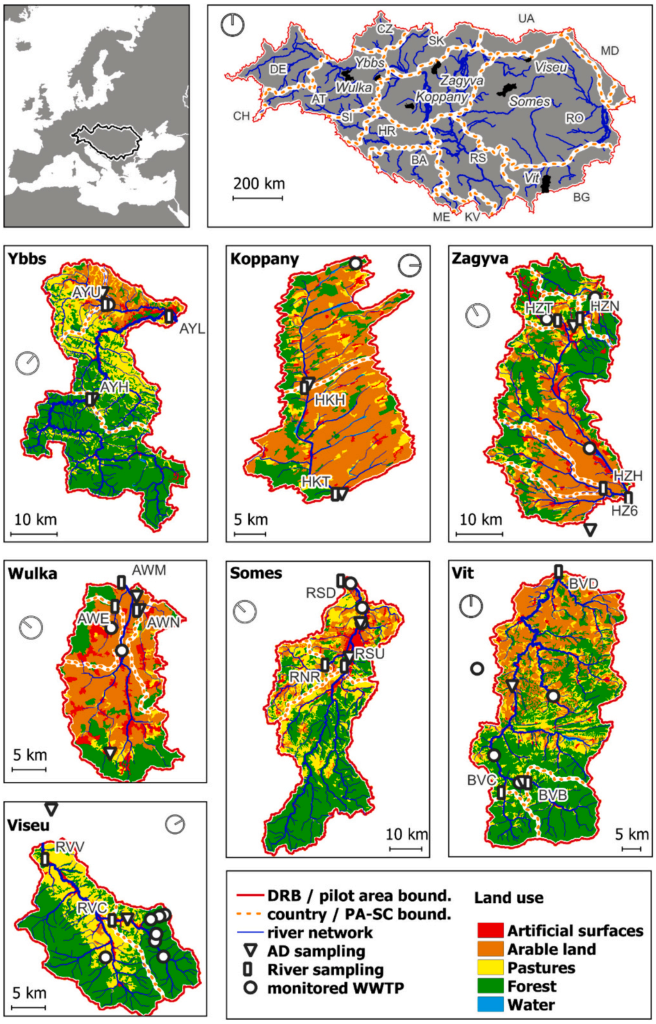

Fig. 1. Map of pilot areas, and their locations in the Danube River Basin. River, atmospheric deposition, and wastewater sampling locations along with main land use classes are indicated. Data sources: Land use: Copernicus Corine Land Cover. River network: ICPDR.

samples that were sent for laboratory analysis. With regard to AD, bulk atmospheric deposition samples were collected until the minimum sample amount was reached, or a period of one month had elapsed. With regard to WW, inflow and outflow were sampled simultaneously, and one-week flow-weighted composites were created by using series samplers. In contrast to aqueous matrices (time composites), for soil, spatial composites were created. Samples were combined based on location (pilot area sub-catchment) and land use. For river low flow, weekly grab samples were combined into composites, each sample representing a bimonthly low-flow condition. For river high flow, flow-proportional high-flow composites were created. Each sample was intended to indicate one high flow event's event mean concentration.

Sampling devices available from the market were partly replaced by low-budget alternatives (e.g. the water sampling device described in (Budai et al., 2020) or the AD sampler described in (Foan et al., 2012)). In the current setting, open bucket samplers were used for AD, the manual grab sampling method was used in the case of river low flow, and various autosamplers along with grab sampling were used for river high flow and WW sampling. Soil samples were collected by tube or auger, see (Jolánkai et al., 2023) for details.

To ensure the comparability of the results, the compounds were analysed in the same laboratory, regardless of the location and pathway of sampling. The collected samples were preserved at the premises of the local partner and sent for analysis to central laboratories via overnight delivery. Further details regarding the sampling programme, sample handling, and laboratory analysis methods and standards can be found in Appendix A3.

2.4. Data evaluation

Lab results along with all relevant information about the sampling were collected centrally and introduced into a pre-designed relational PostgreSQL database (Kittlaus et al., 2023). Collected sampling metadata consisted of location, start and end date, and time of sampling; sampling devices used; long-term mean and actual quantities (rain amount, WW discharge, river flow), and – in the case of river samples – long-term mean as well as actual values of basic water quality indicators such as total suspended solids and electrical conductivity.

A major part of the "Results" section of this paper consists of the analysis of the measurement results, and partly of relating them to location/catchment characteristics. Such calculations/plots were performed using R software version 4.2.2 (R Core Team, 2022). Wherever possible, censored (<LOD, <LOQ) values were replaced with statistical modeling. The modeling was done using "regression on order statistics" as described in (Helsel, 2012) using the NADA R package (Lopaka Lee, 2020), assuming lognormal distribution of the concentrations. For this kind of modeling to be performed, the following two conditions have to be fulfilled simultaneously: (a) the number of uncensored elements $n_{not\ cens} \geq 3$ and (b) the detection rate ≥ 20 %. If statistical modeling could not be performed, censored values were replaced with LOD/2 for PTE and LOQ/2 for other substances before doing any evaluation/calculating statistics. When summing up PAH compounds to calculate ΣPAH16 values censored values were assumed to be 0, and only >LOQ values were considered. If all values to be summed up were below LOQ, then the maximal LOQ was considered. PFOA-equivalents are calculated as the sum product of the 12 PFAS values measured in this study and their respective relative potency factor values as proposed in Annex V. of (EC, 2022c).

Catchment characteristics were assigned to riverine monitoring locations using – wherever possible – pan-European databases, such as Copernicus Land Monitoring Service's Corine Land Cover Map 2018, High-Resolution Layer on Imperviousness (Copernicus Land Monitoring Service, 2020a, 2020b). Economic data were taken from Eurostat: Gross domestic product (GDP) at current market prices by NUTS 3 regions for 2019 (the last pre-COVID year) was used (Eurostat, 2020).

3. Results and discussion

3.1. Lessons learned during implementation of the monitoring program

The successful implementation of the monitoring programme required meticulous preparation. The first step was to collate all available data pertaining to potential pilot areas. In addition to pan-European and large region databases (such as Copernicus and EEA databases, e.g. the UWWTD database), local data (such as hydrology, water uses, and pre-existing measurements on water quality and emissions) was processed. This process facilitated the selection of the sampling locations and the planning of the technical details of the stratified approach. Once decisions had been taken on the sampled pathways and substances, a standard operating procedure was defined. This included all instructions related to sample collection, preparation, and storage, such as the types and materials of sample containers, the addition of preservatives, cooling, and transport. A document was co-edited by the four involved laboratories with guidance from the activity-leading project partner.

Despite the substantial preparatory efforts that were made, a few unexpected challenges had to be overcome during the initial phase of implementation. One such challenge was the negative experiences that were encountered with the originally planned preservation mode for PAH samples, which had to be revised. Another challenge that was

Table 1
Pilot area (PA) characteristics. AD = atmospheric deposition; WW = wastewater; RIV = river water. Data sources: Land use: Copernicus Corine Land Cover; Topography: Copernicus EU-DEM v1.1; Climate, hydrology, point sources and inhabitation: national institutions.

Country, PA name	AT, Ybbs	AT, Wulka	HU, Koppany	HU, Zagyva	RO, Somes	RO, Viseu	BG, Vit
PA outlet point	Greimpers-dorf	Schützen am Gebirge	Tamási	Hatvan	Apahida	Moisei	Disevitza
Outlet point river monitoring station name	AYL	AWM	HKT	HZ6	RSD	RVV	BVD
Catchment area (km^2)	1110	389	660	1210	1960	378	2210
Number of sampling stations AD/WW/RIV	2/1/3	3/2/3	2/1/2	2/3/4	2/3/3	2/1/2	2/4/3
Land use (% of area)							
Forests and natural	57	28	23	44	50	67	49
Pastures	20	1	2	9	17	18	5
Arable land	10	45	63	34	12	0	26
Other agricultural	8	14	9	6	13	10	17
Urban	4	13	3	7	8	4	3
Climate, topography & hydrology							
Mean altitude (masl)	691	256	181	270	380	1126	598
Mean annual temperature (°C)	7.3	9.6	11	12	6.5	3.5	12.6
Mean annual precipitation (mm a^{-1})	1489	695	629	650	700	1200	664
Mean annual flow (m^3 s^{-1})	31.5	1.12	1.26	1.53	18.3	9.07	13.8
Point sources influence							
Inhabitants	76,530	58,516	19,000	110,000	392,000	42,021	51,858
Fraction of WW in river flow (%)	1	39	8	5.7	10	1.6	0.1
Population density (inh. km^{-2})	69	150	29	90	212	112	23

encountered was the importance of glass bottles, which led to the application of low-temperature cooling instead of freezing.

The differing economic potential of the countries also influenced the choice of sampling device. While Austria and Hungary employed autosamplers for river high-flow sampling, Romania and Bulgaria opted for the manual sampling method. This may appear to be a purely technical decision, but analysis of the results indicated that manual sampling of high-flow events was not successful. The difference between low-flow and high-flow values as well as the concentrations was significant for the AT and HU pilot areas, whereas it was insignificant not only in the remote Viseu and Vit catchments but also in the easily accessible Somes catchment. This strongly suggests that autosamplers are unavoidable for proper high-flow sampling.

Conversely, low-budget solutions yielded satisfactory results. Atmospheric deposition samplers were useful for drawing spatial patterns of substances conveyed by atmospheric processes, including some PTE, PAH, and PFAS.

3.2. Spatial patterns in the distribution of PTE, PAH, and PFAS

3.2.1. Comparison of PTE levels across regions

Comparing the level of contamination across the various locations gives insight into the sources and spreading of pollutants. As, Zn, Cd, and Cu are known for being to a significant extent of geogenic origin (Ballabio et al., 2018; Eynde et al., 2023; Tóth et al., 2016). Soil and river water concentration levels of these elements are expected to reflect partly the geogenic conditions. This expectation was fulfilled; in the following, we describe two examples.

Cu, Zn and Cd concentrations in the Viseu River low flow samples outranged those of other PA. Both total and dissolved Zn concentrations in river water samples exceed values of other PA by 3 orders of magnitude. Cu levels at station “RVC” exceed those at other locations by 2 and 1 order(s) of magnitude in the total and the dissolved phase, respectively. Cd also indicated very high values. In addition, As and Pb indicated elevated total concentrations whereas Ni indicated elevated dissolved concentrations in river low-flow samples, again, especially in the upper sub-catchment (“RVC”). This is due to the improper/missing treatment of drainage effluents from abandoned mines, as already documented by (Bird et al., 2010; Buteana et al., 2014; Krutilla and Logan, 2009; Macklin et al., 2003). In addition, besides the two highly urbanized sub-catchments “AWE” and “HZT”, the whole Wulka and Koppany PA (both characterized by >50 % agricultural land use) indicated elevated concentrations of dissolved Cu suggesting that besides urban areas, agriculture is also an important source of this substance (Fig. 1).

As another example, the four PA located in the Pannonian Region (Wulka, Koppany, Zagyva, and Somes) indicated elevated concentrations of As both in river water and in AD samples compared to the other PA. The reason is suspected to lay in the higher geogenic As concentration in this region, which has been documented previously (Rowland et al., 2011; Srivastava, 2020; Varsányi and Kovács, 2006). Regarding concentrations measured in river water samples: in the Koppany and Zagyva PA, dissolved As concentrations were higher during low flow periods than during high flow events whereas in the Ybbs and Wulka regions, it was the other way round. This again underlines the elevated geogenic As concentrations in the Carpathian Basin and also indicating that bedrock is the dominant source of this substance. Surprisingly, soil samples only partly exhibited the pattern: on the Wulka and the Somes, As concentrations in soil samples were high, but on the Koppany and the Zagyva, they were in the usual range.

The concentration of PTE in river high-flow samples of the Koppany PA outrange those of samples from most other PA. Most spiking is the concentration of Ni, and especially Cr in the unfiltered river high flow samples: they exceed those in other locations by 2 orders of magnitude. In addition to the already mentioned elements, Cu, Cd and Pb also indicated elevated concentrations in the Koppany river high-flow unfiltered samples. In particular, when sorting high flow event samples by the concentration of suspended solids, the first three are from station HKH, with values an order of magnitude higher than the highest values from the other locations. An explanation for that might be that the suspended solid concentration of a few high-flow events was extremely high compared to that of other locations. Besides the high erosivity of this region, the reason for elevated suspended solids concentration is also the functioning principle of the applied high-flow sampler. Namely, in several cases, the sample collection had to be stopped before the end of the flood event because the sample container got filled too early. We hypothesize that Cr and Ni originate from wastewater sludge washed off the banks during such high flow events, see earlier in this section. Relatively high concentration of these elements in river water Tot samples divided by suspended solid concentrations corroborates this hypothesis (see Fig. A4).

In addition to the PTE of geogenic origin, a second group of PTE is capable of indicating anthropogenic sources of pollution. While Hg is known for being emitted into the atmosphere in large amounts during fossil fuel burning, Cr and Ni are accounted for as becoming into the environment predominantly with wastewater discharges (Ballabio et al., 2021; Tóth et al., 2016). When evaluating the results of the monitoring program, it was found, that the concentration of Hg was higher in the Zagyva AD and the Koppany, Zagyva, and Somes river low flow samples as in samples of the respective pathways of the other PA. The reason is suspected to lay in coal-fired power plants and/or biomass-burning activities located in these regions. Regarding the Zagyva PA, natural gas and coal power plants are located a few tens of kilometers from one of the AD sampling sites.

3.2.2. *Comparison of PAH levels across regions*

Most PAH forms were above average in the Wulka and Ybbs river water samples. The Zagyva and the Vit PA exhibited the highest, while the Ybbs, the Somes, and the Viseu had the lowest AD concentrations.

PAH were ubiquitous in soils (12 out of 16 compounds were found in quantifiable amounts in all PA), however, with a large spatial variability. For most compounds, the Wulka indicated the highest level of contamination, followed by the Ybbs and Zagyva PA, while in the Koppany, Somes, Viseu, and Vit PA, a significantly lower level of contamination was present. Forests indicated higher concentration levels than pastures and agricultural soils. We hypothesize that the tendencies between land use types reflect legacy pollution: atmospheric PAH were adsorbed on leaves (forests have leaf area indices much higher than crops), and after falling they become soil (Bossert and Bartha, 1986; Plachá et al., 2009), see also Ch. 0.

A long list of literature resources suggests, that PAH isomer ratios are capable of indicating whether they originate from pyrolytic or petrogenic sources (Glendell et al., 2018; Mali et al., 2022; Yunker et al., 2002). By analyzing soil data of the Wulka, Koppány and Zagyva PA, (Jolánkai et al., 2023) already pointed out that the primary source is most likely residential heating. Based on the Fla / (Fla + Pyr) ratio, this does hold for all seven PA. The Fla / (Fla + Pyr) ratio was between 0.44 and 0.67 for the AD samples, with the Ybbs indicating the lowest value, and the only value below 0.5; the Viseu indicated the highest value. Ind / (Ind + BghiP) ratios were between 0.43 and 0.46 in soil samples of all seven PA indicating wood and coal combustion and/or petrochemical fuel combustion being the source of the PAH. Due to the low detection rate, the isomer ratios could not be calculated for pathways other than soil and AD.

3.2.3. *Spatial patterns in PFAS contamination*

As indicated in Tables A3-A4, detection and quantification limits were ca. one order of magnitude lower for PFOS and PFOA than for other PFAS. As a consequence, detection rates were much higher for the two most commonly investigated PFAS than for the others. In particular, a cross-PA evaluation could only be done for these two PFAS for pathways other than soil. In soil, however, almost all PFAS could be detected in most PA (8 substances out of 13 were mostly above LOQ, with the higher (>10) C-number PFAS missing).

Across pathways and substances, the following tendency can be observed: concentration of PFAS decreases from northwestern to southeastern PA from the order of magnitude of 10^{-2} to the order of magnitude of 10^{-4} mg l^{-1} in river water and from 1 to 0.1 μg kg^{-1} DM in soil. The pattern is best visible for the soil pathway and somewhat more marked for PFOA than for PFOS. However, in the case of the river water samples, the Ybbs PA breaks the above pattern and behaves as an outlier: it exhibited significantly lower concentrations in river water samples than the Wulka, and slightly lower concentrations than the Hungarian PA both for PFOA and PFOS (see Figs. A8-A10).

Comparing concentration levels by sub-catchment, a secondary pattern can be observed: in areas with higher urban influence, concentrations are higher. This secondary pattern, however, does not override the above-described geographical tendency drawn between PA. In particular, stations “AYU”, “AWE”, “HKH”, “HZT” and “RSD” exhibited higher concentrations of PFOA in river water samples than other stations on their respective PA. The mentioned stations can be characterized (1) either by a fraction of agricultural land that exceeds other sub-catchments on the respective PA or (2) with a fraction of WW that exceeds other sub-catchments on the respective PA. This suggests that – just like PTE and PAH – PFAS can also be regarded as ubiquitous contaminants that can originate from various diffuse and point-like sources of contamination.

Regarding the soil samples, PFAS contamination levels significantly differed by land use: similar to PAH, forest soils exhibited the highest mean concentrations, while pastures and agricultural areas exhibited lower levels, see also Section 3.7.2.

3.2.4. *PAH and PFAS concentrations during low-flow and high-flow periods by location*

PA-wise comparison of pathway mean concentrations enables for tracking the sources of contaminants. Wherever soil and AD concentrations were low compared to WW concentrations, the main source is the WW implying that river low flow concentrations are higher than river high flow ones (examples: Naph in all Austria and Hungarian PA, Phen, ∑PAH, and PFOS in the Hungarian PA). On the other hand, in PA where WW concentrations were low compared to AD and soil, the primary source is diffuse leading to elevated concentrations during high flow events compared to low flow periods. Examples are Phen, Fla, ∑PAH in the Wulka, and PFOS in the Ybbs. The comparison also highlights the combined cases: where both types of sources have an impact: PFOA concentrations in the Wulka River water samples are the highest among all PA, and both diffuse and WW sources have a significant role in this. Similar is the situation with PFOA in the Ybbs PA, although the pollution here results in lower river water concentration obviously due to higher dilution due to higher runoff. Interestingly, on both Austrian PA, the highest river high flow PFOA concentrations are indicated by the sub-catchments with the highest fraction of agricultural land (“AWE” and “AYU” in the Wulka, and Ybbs PA, respectively).

There is no real difference between low flow and high flow concentrations regarding the two intermediate PAH forms Phen and Fla when aggregated over all PA (ratio of high flow to low flow mean values are between 90 and 100 %). This, however, masks some spatial patterns which are most visible when comparing station-wise mean values from the Wulka and the Koppany PA. At stations “AWE” and “AWM”, the concentration of ΣPAH16 and especially Phen is higher in high flow than in low flow while it is the other way around on the Koppany and Zagyva stations (ratio of PA-wise mean high flow to low flow Phen concentration values is 1.42 and 0.73 on the Wulka and Koppany, respectively). The reason behind is supposed to lay in the source of the PAH: on the mentioned Wulka stations, it is supposed to be more the AD and the soil while on the Koppany, it is more the WW (mean Phen concentration in AD/WW is 20.7/9.8 and 12.8/25.9 ng/l in the Wulka and Koppany, respectively.) The unique Ybbs stations behave controversially: at station “AYU” high flow to low flow Phen >1, at “AYL”, ratio < 1 was calculated. This latter might be due to higher suspended solids values at “AYU”: it exhibited the highest suspended solids values in the PA. Underlying reasons for the other PA can be multiple-fold (composition of WW in the unique WWTP, presence/absence of industrial dischargers, composition of atmospheric PAH emissions, or the – already mentioned – malfunctioning of the Koppany WWTP) (Fig. 2).

3.3. *In-depth analysis of two pairs of headwater sub-catchments*

The two Wulka sub-catchments “AWE” and “AWN” are located next to each other, characterized by similar size (67 and 62 km^2, respectively) and similar geographical characteristics but different hydrologic conditions and anthropogenic influences. In particular, the mean annual

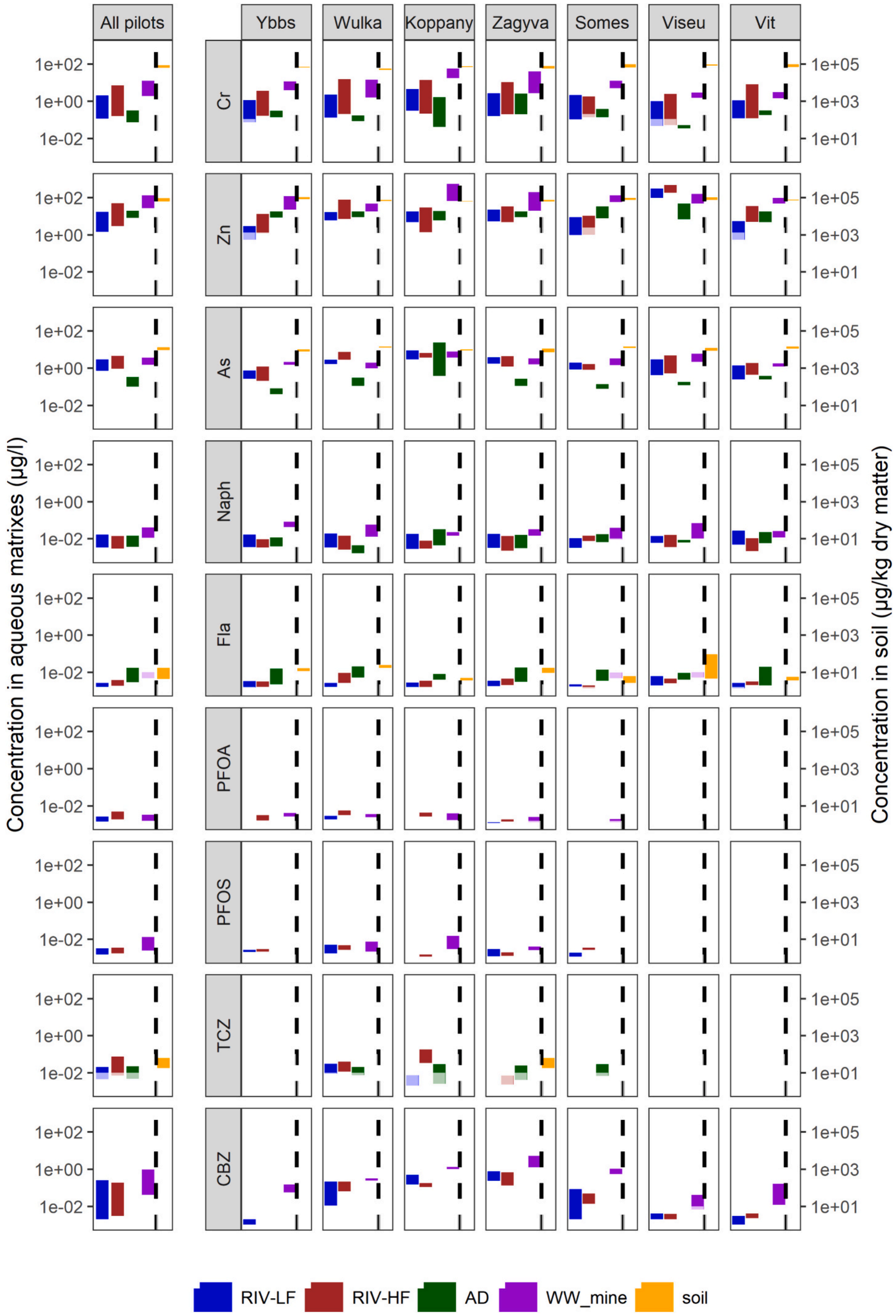

Fig. 2. Variation of concentrations across the pilot areas. Aqueuos matrixes: RIV-LF: river low flow; RIV-HF: river high flow; AD: atmospheric deposition; WW_mine: wastewater and mine effluents. Solid matrix: soil.

river flow at the sub-catchment outlet is 0.19 $m^3 s^{-1}$ at the “AWE” station while at the “AWN”, it is 0.09 $m^3 s^{-1}$. The sub-catchment “AWE” is characterized by 30 % forests, 52 % agricultural land, and 17 % artificial surfaces whereas on the “AWN”, the numbers are 19 %, 69 %, and 12 %, respectively. In addition, the “AWE” catchment is characterized by a high fraction (49 %) of treated wastewater in river flow whereas in the “AWN” sub-catchment there are no WW discharges. A general expectation therefore is that “AWE” will exhibit equal or higher concentrations of anthropogenic pollutants emitted through urban pathways than “AWN”.

The concentration of almost all PTE is higher or equal in the “AWE” river samples compared to “AWN”. It holds for both high flow and low flow, total and dissolved phases. Particularly, Ni, Zn, and Pb are higher in river low-flow samples in the dissolved phase at “AWE” than at “AWN”, supposedly either due to current WW discharges or due to legacy pollution (Fig. 2).

Similar to the “AWE” - “AWN” pairing, the 74 km^2 “HZT” sub-catchment can be contrasted to the 158 km^2 “HZN”. While sizes are comparable, the share of forests and agricultural areas on the catchment as well as runoff in the same range (58–70 %, 22–23 %, and 72–83 mm a^{-1}, respectively), the former is characterized by a significantly higher share of artificial surfaces (19 % as opposed to 7 %) and fraction of WW in the river (24 % contrasted to 0.7 %). A general expectation, therefore, is, that “HZT” will exhibit equal or higher concentrations of urban- and wastewater-originated pollutants than “HZN”.

Indeed, the total concentration of all the PTE except As was two to three times higher in the low-flow samples at "HZT" than at "HZN", whereas dissolved concentrations were one to five times higher in the more urbanized sub-catchment. On the other hand, the high flow samples were – for the substances total Cr, total Ni, and total As – more concentrated at "HZN" than at "HZT", whereas for the rest of the pollutants, no substantial difference was found.

Whereas most substances show the same pattern in the Wulka and the Zagyva pairs of subcatchments: elevated dissolved concentrations in the low-flow samples of the more urbanized subcatchments compared to the less urbanized one; complemented with similar or elevated total concentrations in high-flow samples of the less urbanized subcatchments compared to the more urbanized ones. However, this does not hold for As. The concentration of this substance was found to be higher in the "AWN" river samples compared to "AWE" in low flow samples (both total and dissolved phase) and high flow samples in the dissolved phase. On the contrary, the total high flow concentrations were higher in the "AWE" catchment than in the "AWN". This gives insight into the fate this substance undergoes: normally "clean" (As-free) urban surfaces are "polluted" by wind carrying local dust; this is then washed off during rainfall events, causing elevated total concentrations in river high flow samples. The consequences are higher in the "AWE" catchment due to the higher share of artificial surfaces. As a parallel process, As is also leached out from the bedrock via subsurface flow; the lower runoff values result in higher concentrations in the baseflow. Since the town Salgótarján is located in a rather closed valley less prone to wind, low flow concentrations were comparable in the "HZT" sub-catchment to those in the "HZN", whereas total high flow concentrations were higher in the "HZN" sub-catchment, compared to "HZT".

Regarding PAH, the 2 × 2 headwater catchments in the Wulka and Zagyva PA lead to interesting findings. Naph shows a lower tendency to attach to suspended solids and is thus diluted during high-flow events. Fla is the opposite in all sub-catchments, although to a variable extent. However, Phen (indicating intermediate properties) indicated high flow: low flow ratios >1 on the Wulka and ratios <1 on the Zagyva. The cause is hypothesized to lay in the source of the PAH. On the Zagyva, it is supposed to be more the WW, and on the Wulka, the AD (see also Figs. A5-A7).

3.4. Pesticides

Considering their land cover / land use characteristics, the sub-catchment can be classified into three categories. (i) The dominance of forest land use ($>$55 %) characterizes the sub-catchment "AYH", "HZN", "HZT", "RSU", both Viseu sub-catchments ("RVC" and "RVV") and the two headwater Vit sub-catchments "BVB" and "BVC". (ii) Dominance of agricultural land use (min. 50 %, usually around or above 60–70 %, with forests $\leq$30 %) characterizes all Wulka, all Koppany, sub-catchments along with the sub-catchment "AYU", "HZH", "RNR" and "RSD". (iii) On a smaller portion of the sub-catchment, dominant agricultural land use (40–60 %) is complemented by high fraction of forests (40–60 %): sub-catchment "AYL", "HZ6", and "BVD" belong to this category. The above categorization is well depicted by the fact that detection rate $>$ 50 % of any pesticide/metabolite in any pathway is shown only by the latter two categories. In sub-catchments, where agriculture occupies $<$50 % of the catchment area, pesticide detection rates were $<$50 % in all pathways. To refine: Met and TCZ were detected in $>$50 % of river high flow samples in sub-catchments of category (ii), whereas the metabolites also appeared in river low flow samples at more downstream sampling stations (e.g. "AYL"). Only the raw forms Met and TCZ appeared in AD or soil samples: the former in 50 % of the soil samples of the Koppany whereas the latter in 60 % of the Zagyva soil samples and both in ~70 % of the Wulka AD samples (see Figs. S10 and S11).

The raw forms Met and TCZ show rather high intra-stational temporal variance, and exhibit higher concentrations in river high flow than in river low flow samples for each PA where they were detected. On the contrary, the metabolites Met-ESA and Met-OA are more balanced throughout seasons and flow conditions. Wherever it could be evaluated, high flow to low flow ratios were above 1 for Met and TCZ meaning elevated concentrations during high flow events. In the contrary, for the metabolites, high flow to low flow ratios were partly above, and partly below one. On the Koppany, the high flow to low flow ratios for Met and TCZ were between 8 and 190 (i.e. 190 times higher mean concentration of Met at HKH during high flow events than during low flow periods); while it was between 2 and 15 for Met-ESA and Met-OA.

There is an ongoing argument throughout scientific literature, that in-stream pesticide concentrations are highly variable, and thus targeted monitoring is needed to detect representative concentrations (Chow et al., 2023; Holvoet et al., 2007; Moser et al., 2018). Similar statement holds for spatial variability, the solution to which is mostly formulated as the need to collect pesticide application data to the highest possible accuracy (Fabre et al., 2023; Umweltbundesamt, 2019; Warne et al., 2023). However, the difference in behavior between base products and metabolites – although reasonable – has, to our knowledge, not yet been documented.

3.5. Pharmaceuticals

Due to low development of wastewater collection and treatment infrastructure in the Vit catchment, data from BG are not included in this subsection.

Pharmaceuticals were expected to show up in wastewaters and rivers receiving wastewater discharges. Wastewater inflow values were 2.2 ± 1.9 and 4.5 ± 2.7 $\mu g\ l^{-1}$ for CBZ and DCF, respectively. Samples were taken during dry weather conditions to avoid minimal dilution by rainwater in the sewer system. According to our measurements, neither of the pharmaceuticals included in this study is removed to remarkable amounts in the studied plants. Concentration values vary within an order of magnitude for DCF and two orders of magnitude for CBZ across locations (treatment plants), and it is hard to find a strong spatial pattern, although it seems that concentrations in Hungary are somewhat higher than those in the neighboring countries, especially for CBZ. Raw wastewater values indicated a weak seasonal pattern. Concentrations were somewhat higher in summer and lower in spring and fall (no samples were taken during winter), especially for CBZ. This might be due to the dilution of wastewater during periods with more rain.

Capita-specific rates (i.e. concentration multiplied by wastewater flow and divided by the number of inhabitants) were more uniform than the raw concentrations. Regarding CBZ, inhabitant-specific emissions were found to be 0.34 ± 0.23 and 0.31 ± 0.22 mg/cap/day to and from the WWTP, respectively. The same values for DCF were 0.92 ± 0.53 and 0.68 ± 0.33 mg/cap/day. Capita-specific emission values allow for further inspection of spatial patterns. DCF values are uniform across countries, but CBZ seems to indicate somewhat lower concentrations at AT plants than in HU (Fig. 3).

Interestingly, in the river water samples, almost the same inhabitant-specific values can be discovered, but with higher uncertainty. Inhabitant-specific emission rates calculated from river low flow samples are 0.65 ± 0.76 and 0.78 ± 0.96 mg/cap/day for CBZ and DCF, respectively. All values are in the same range as those calculated from the WW samples. Also, it was observed, that from river high-flow samples, larger inhabitant-specific values were calculated than from river low-flow samples, which suggests, that even these substances tend to – to some extent – accumulate in bottom sediment and are resuspended during high-flow events. Inhabitant-specific values calculated from river water samples also indicate the light pattern: lower emissions in AT compared to HU for CBZ (AT: 0.43 ± 0.45, HU: 0.80 ± 0.88 mg/cap/day).

In addition to the seasonal pattern, a spatial pattern is also to be found. Regarding pharmaceuticals, country-wise mean values range over an order of magnitude both for river water and WW samples. As a rule of thumb, Hungary shows the highest, while Bulgaria the lowest mean concentrations of carbamazepine. While WW samples are more

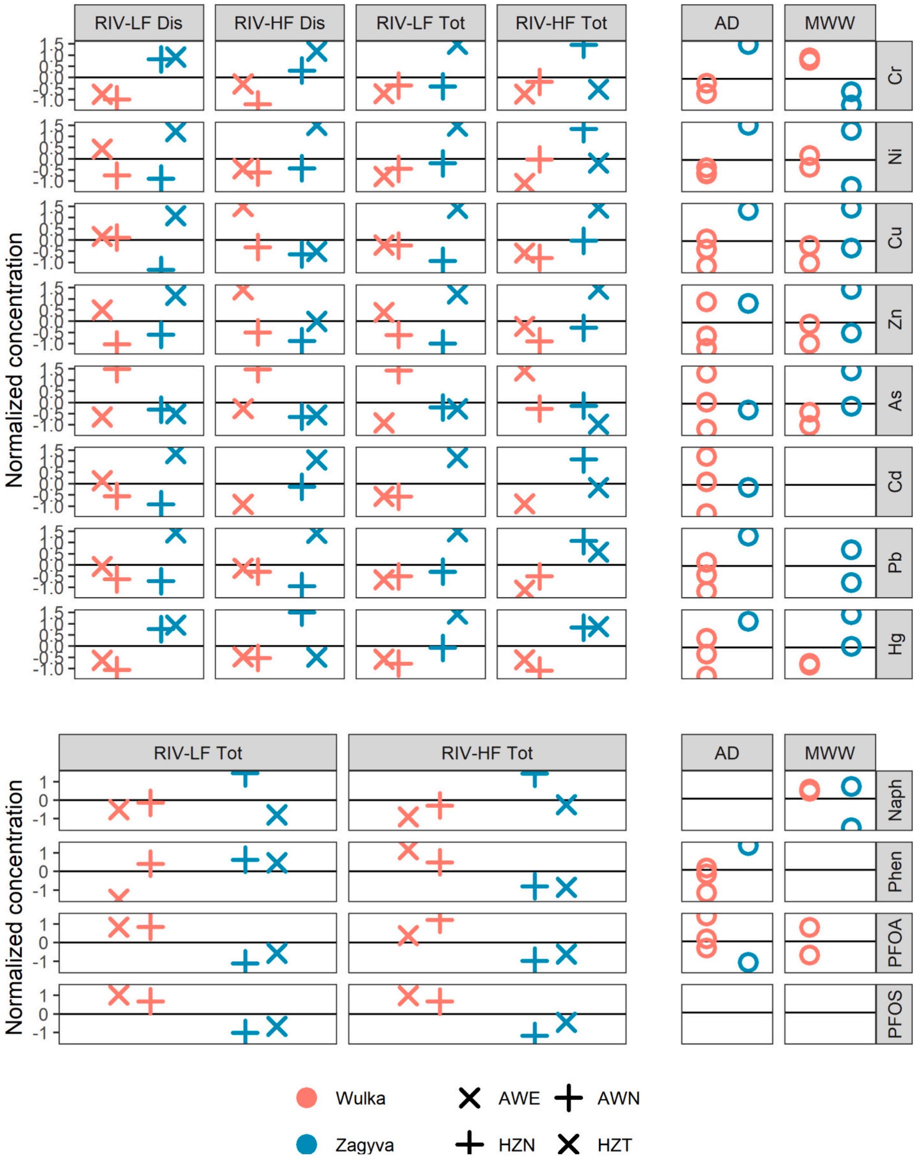

Fig. 3. Normalized concentration of PTE, PAH, and PFAS across pathways. Normalization means subtracting group mean and dividing by group standard deviation. RIV-LF: river low-flow; RIV-HF: river high flow; AD: atmospheric deposition; MWW: municipal wastewater; Dis: dissolved phase (filtered samples); Tot: total phase (unfiltered samples). See Fig. 1 for the names of the sampling sites (AWE, AWN, etc.).

immediate indicators of pharmaceutical contamination, river water samples show a "composite" of the catchment. This is well reflected when plotting river water concentrations against the fraction of WW. Regarding both CBZ and DCF, Hungary indicated larger whereas Austria had lower concentrations. For CBZ, Romania lay in between whereas for DCF, it lay next to Hungary. In each country, DCF shows higher levels than CBZ, especially in Romania. In particular, DCF concentrations were 2.2 ± 1.1, 5.2 ± 2.9, and 1.9 ± 1.8 for AT, HU, and RO, respectively whereas those of CBZ were 0.16 ± 0.099, 2.9 ± 1.8, and 0.86 ± 1.03 for the same countries. So the real difference is in CBZ for AT: it's much lower than the other two countries. For DCF, there is no significant difference. Regarding concentrations, not only the differences in pharmaceutical consumption might lie in the background. Due to relatively high drinking water prices in Hungary, drinking water consumption is law, and wastewater is concentrated (Patziger, 2017).

3.6. Dynamics in river water concentrations

Stratifying the river sampling by flow situation, that is: distinguishing between high-flow and low-flow conditions empowered insights into the behavior of the various pollutants. As already mentioned, only in the Ybbs, Wulka, Koppany, and Zagyva catchment was the difference between river high flow and river low flow values found to be significant. So, in the following, when contrasting concentrations during high flow events to those during low flow periods, only data from these PA are included. (For station "HZH" only one high flow sample was available.) Higher concentrations of substances emitted from impervious areas or diffuse emissions, especially those that are particle-bound, were expected in high-flow samples. In the contrary, a lower concentration of substances emitted primarily via WWTP was expected such as for pharmaceuticals.

Due to the tendency of PTE to attach to small particles, high-flow total concentrations were expected to be higher than low flow total concentrations. This was found for all heavy metals in the total phase, except for As at stations "HKT", "HZT", and "HZ6". These two stations have rather small dynamics: "HZ6" is the outflow point of a part of the Zagyva catchment, a large portion of which is rather flat. As such, subsurface flow pathways play a relatively important role. The catchment belonging to station “HKT” includes many retention reservoirs causing that (1) high flow events are not necessarily associated with rainfalls (e.g. artificial emptying of reservoirs with cleaning purposes) and (2) rainfalls don’t necessarily cause high flow events, e.g. due to retention in reservoirs. There is a difference in the order of magnitude of the high flow to low flow ratios both across locations and across substances. From the stations, “AYU”, “AYL”, and “AWM” indicated the highest, while stations “AWE”, “AWN” and “HZT” the lowest high flow to low flow ratios. From the substances, Pb and Cr indicated the highest, while As, Zn, and Ni the lowest high flow to low flow ratios. Not every aspect of these differences has an apparent explanation. Lower ratios appeared at sub-catchments with a relatively high fraction of artificial surfaces, indicating that pollution in these locations comes mainly from permanent sources (e.g. wastewater discharges). The difference in the pattern between Ni and Cr is unexpected, these substances usually show similar patterns (Fig. A3). Most dissolved PTE however (except for Cu, Hg and As in some locations) indicated lower concentrations in river low-flow samples compared to river high-flow (Fig. 4).

Regarding PAH, only the first six (Naph, Ace, Fluo, Ant, Phen, Fla and Pyr) were detected in river waters. The largest among them, i.e. Fla, and Pyr, indicated elevated concentrations during high flow events (compared to low flow periods). These are the larger molecules. The lower ring number and lower molecular weight PAH (Naph and Ace) are diluted during high-flow events. In particular, high flow to low flow ratios were between 41 and 64 % for Naph and Ace and between 124 and 241 % for Fla and Pyr. According to the literature, the lower (2–3) ring number compounds Naph, Ace, Acy, Fluo, Ant, and Phen have a molecular weight < 200 g mol^{-1}; lower octanol-water partitioning coefficient and lower organic carbon partitioning coefficient logKoc <4.2 meaning a higher tendency to dissolve in water and a lower one to attach to organic matter. These forms were detected in most river water and AD samples, but only <50 % of the soil samples. In the contrary, higher (>3) ring number compounds (BaA, Chry, BbF, BkF, BaP, DahA, BghiP and Ind123cdP) have a molecular weight > 220 g mol^{-1}, a lower tendency to dissolve in water, and a higher one to attach to organic particles. They were almost ubiquitous in soils but only rare in river water and AD. Thus, the intermediate group (Fla and Pyr) are capable of indicating the fate and spreading: These were detected in a relatively high number of river water, AD, and soil samples. The reflection of hydrophobicity in the detection rate/concentration ratios of different compartments is in accordance with previous publications (e.g. Chiffre et al., 2015; Zoboli et al., 2019).

PFAS (except for the sulfonic ones) indicated the pattern of higher concentrations during high-flow events. PFBS and PFOS, however, indicated lower concentrations in river low-flow samples compared to river high-flow. Further, the pesticide metolachlor also indicated the pattern (namely higher concentrations during high flow events). Due to <LOQ values in low-flow samples, high flow to low flow could not be calculated for tebuconazole. However, detection rates were higher in high-flow samples than in low-flow ones, so the same pattern is indicated as for metolachlor. Due to the dilution effect, lower concentrations were expected for substances emitted primarily via municipal WW, such as pharmaceuticals. This expectation was also fulfilled: high flow to low flow mean concentrations were 0.63 and 0.58 for CBZ and DCF, respectively.

For most substances, it is problematic to expect clear differences between high flow and low flow values, because they originate from many different sources and reach surface water through several pathways. For these contaminants, two simultaneous effects: (1) more emissions from impervious and agricultural areas during runoff and (2) more dilution of time constant emissions like WW discharges due to rainfall-runoff can result in various concentrations. Substances in this group are Ni, Cr, Hg, Pb, Phen, and PFOS. A detailed investigation (e.g. distinguishing between pilot areas based on catchment land use, e.g. screening out pilot areas with significant agricultural share for Met) might deliver interesting figures for these substances, too.

3.7. Experimenting with functional relationships between concentrations and catchment characteristics

3.7.1. River concentrations

To summarize and generalize the above: the highlighted substances, i.e. Ni, Cu, Zn, As, Fla, Pyr, PFOA and Metolachlor are suspected to originate from diffuse sources, and delivered to the rivers during runoff events or remobilized in them during high flow situations. To test this hypothesis, sampling location wise high flow mean concentrations were plotted against the relative importance of impervious and agricultural areas in the respective sub-catchments and linear regression lines were plotted (Fig. 5). Another assumption behind the hypothesis is that diffuse emissions are uniform over the PA. The plots reveal various relationships. Neither of the PTE exhibit a strong relationship with any of the catchment characteristics, which suggests that neither of the mentioned surfaces dominates its behavior. This does not mean, that they are not a significant source, but other processes (be they emission sources or transmission processes) have at the same or higher influence on the riverine concentrations. Zn indicated a somewhat stronger correlation with the share of impervious areas, which indicates the dominance of these surfaces over the agricultural ones in the emission of Zn. However, the correlation is weak, so other sources/processes might have important influences, too. Ni exhibited an almost significant, but weak relationship with agricultural areas, which suggests, that agricultural areas are one of the important sources of this substance. Other major sources include industrial activities. For As, it is the other way round: the fraction of arable land dominates over impervious areas, which corroborates the importance of the already stated emissions sources (geogenic) and processes (erosion primarily by water, secondly by wind) regarding this substance.

Both investigated (“intermediate”) PAH: Fla and Pyr exhibited correlations with impervious shares; this suggests, that – although these substances spread through the atmosphere – urban sources like internal combustion engines and residential biomass burning are dominant over e.g. crop burning and other sources. Still, the relationship is not significant. The only significant relationship was found between impervious areas and PFOA. Although the fraction of arable land uses in the catchment also indicated a positive relationship with the high flow mean PFOA concentrations, the importance of urban surfaces is relatively higher. PFOA is ubiquitous and tends to attach to particles, but the sources are dominantly located in urban areas. Unfortunately, there was not enough data to evaluate any relationship between metolachlor and the share of arable land in the catchment. Also, pesticide usage highly varies by region and is determined by the crops produced and the market situation (e.g. dominance of one company over the other).

Substances originating from permanent point sources are diluted during high-flow events. If the permanent point sources are related to residential activities (like e.g. pharmaceutical consumption and urination), and per capita urination values are uniform over the investigated area, then in-stream concentrations are expected to correlate with the number of inhabitants per water flow, or be inversely proportional to the so-called dilution potential of the river (i.e. the long term mean river flow per the number of inhabitants in the catchment). In the bottom-most row of Fig. 5, some examples are plotted. Naph shows no correlation because it is related to industrial sources rather than to residential ones. PFOS, CBZ, and DCF, on the contrary, indicated significant correlations meaning that they dominantly originate from residential sources (and also, either that they are not screened out at the WWTP, or that they are uniformly removed). DCF indicated a higher correlation than CBZ: in Section 3.5 we already showed that per capita DCF emissions are more uniform across pilot areas than those of CBZ.

3.7.2. Soil concentrations

The applied soil sampling approach (combining stratified random samples to composites by land use categories) proved to be successful in terms of value and spatial representativity of the contamination levels.

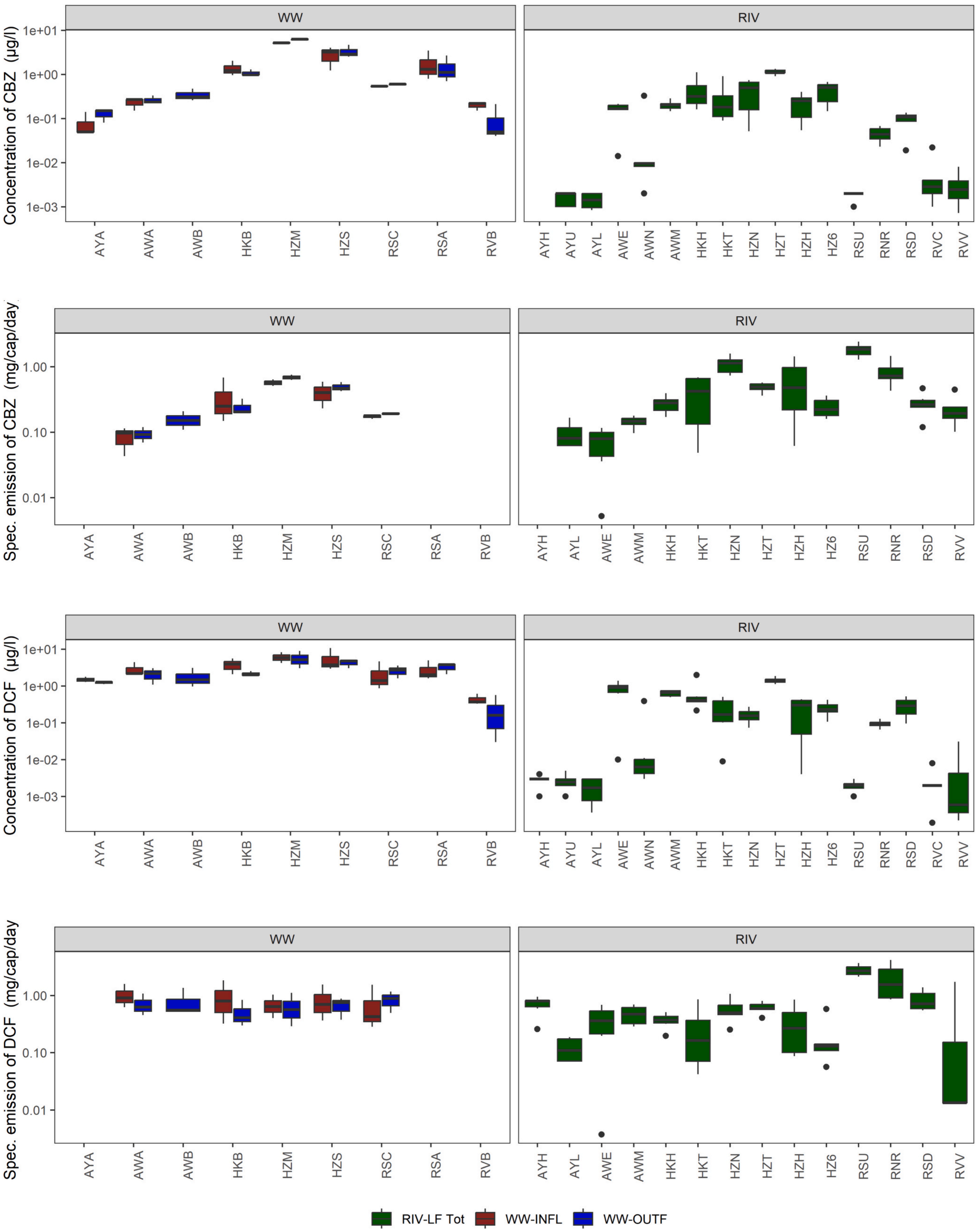

Fig. 4. Measured concentrations ("conc.") and derived specific values ("spec. em.") of the pharmaceuticals: carbamazepine (CBZ) and diclofenac (DCF) in wastewater treatment plant in- and effluents ("WW") and river water ("RIV") samples. RIV-LF Tot: River low-flow total (unfiltered) concentrations; WW-INFL: wastewater plant inflow; WW-OUTF: wastewater plant effluent. AYA, AWA, AWB, etc. denote the sampled plants, see Fig. 1.

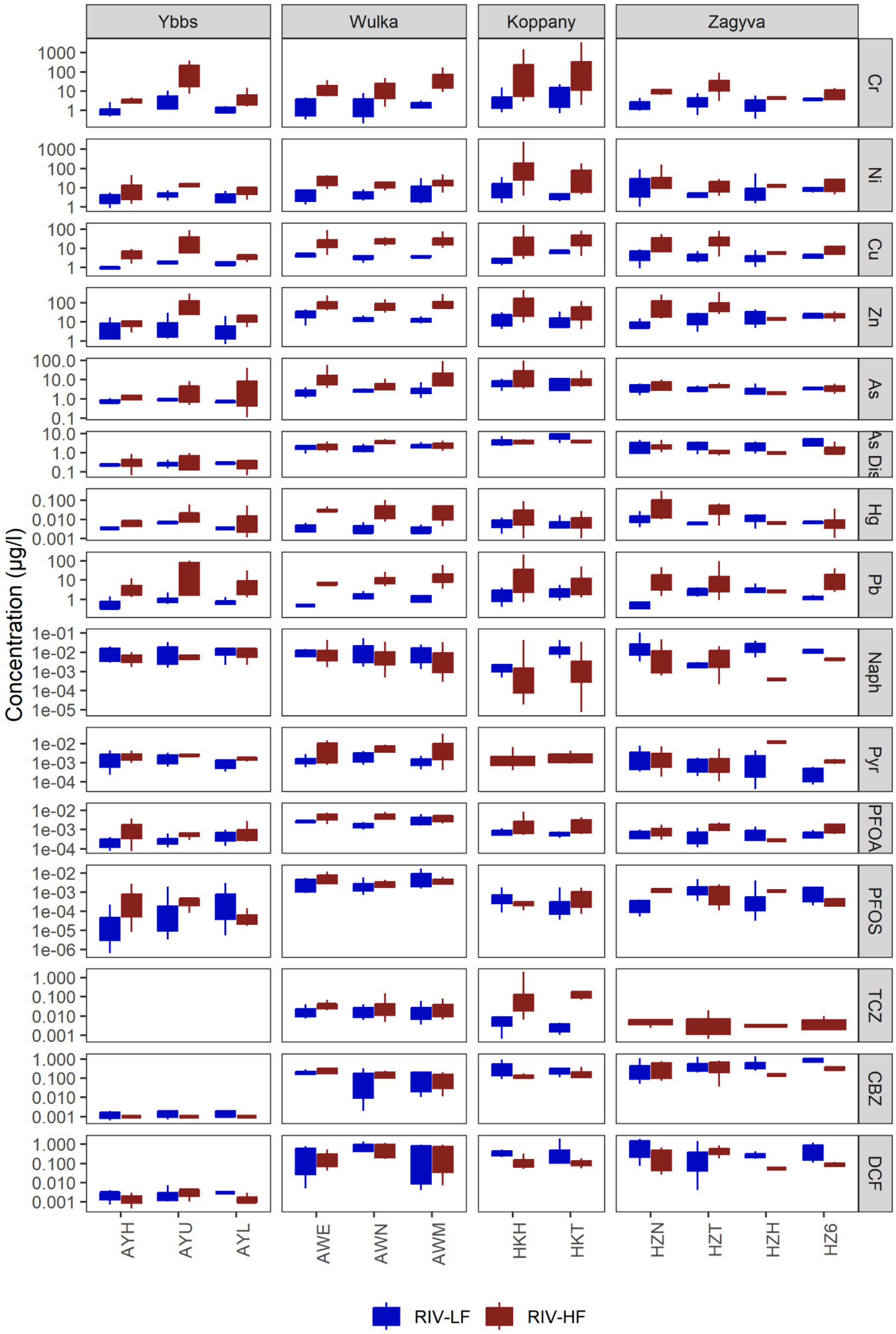

Fig. 5. Ranges of concentration for various substances during high flow events (brown) and low flow periods (blue). Boxes the interim half of the data (25 % - 75 %). RIV-LF: River low-flow; RIV-HF: river high-flow. AYH, AYU, AYL, etc. denote the sampling sites, see Fig. 1.

Observed concentration ranges highlighted large spatial variability across the DRB.

First, a difference can be observed when country-wise plotting the soil concentrations: there is a trend between the countries, but it does not point in the same direction for all substances. While the concentration of PTE slightly increases, the concentration of PAH and PFAS strongly decreases from northwestern to southeastern countries. The reason behind this is suspected to be the difference in economic development of the particular areas.

Second, the already mentioned between-land-use differences can be observed in each country. In particular, the concentration of PTE increases, whereas the concentration of PAH and PFAS decreases from forest through pasture to agricultural soils. The differences are lower for PTE and larger for PAH and PFAS; the reliability of the trends should be regarded as high due to the composite sampling approach (Fig. 6a-e).

Inspired by the above, we plotted mean soil concentrations by PA against the GDP of the PA, and found strong relationships for ΣPAH and PFOS ($R^2 > 0.6$, *P*-value <0.05). In a second step, mean river high flow concentrations were plotted against GDP per PA, leading to even stronger relationships for ΣPAH, PFOA, and PFOS ($R^2 > 0.86$, P-value <0.01). This highlights, that pollution of soils and other surfaces is in a strong relationship with the economic potential of the area; however, larger specific runoff will dilute the contamination (Fig. 6f-j).

3.7.3. Implications for modeling

Based on the above, the following conclusions can be drawn for

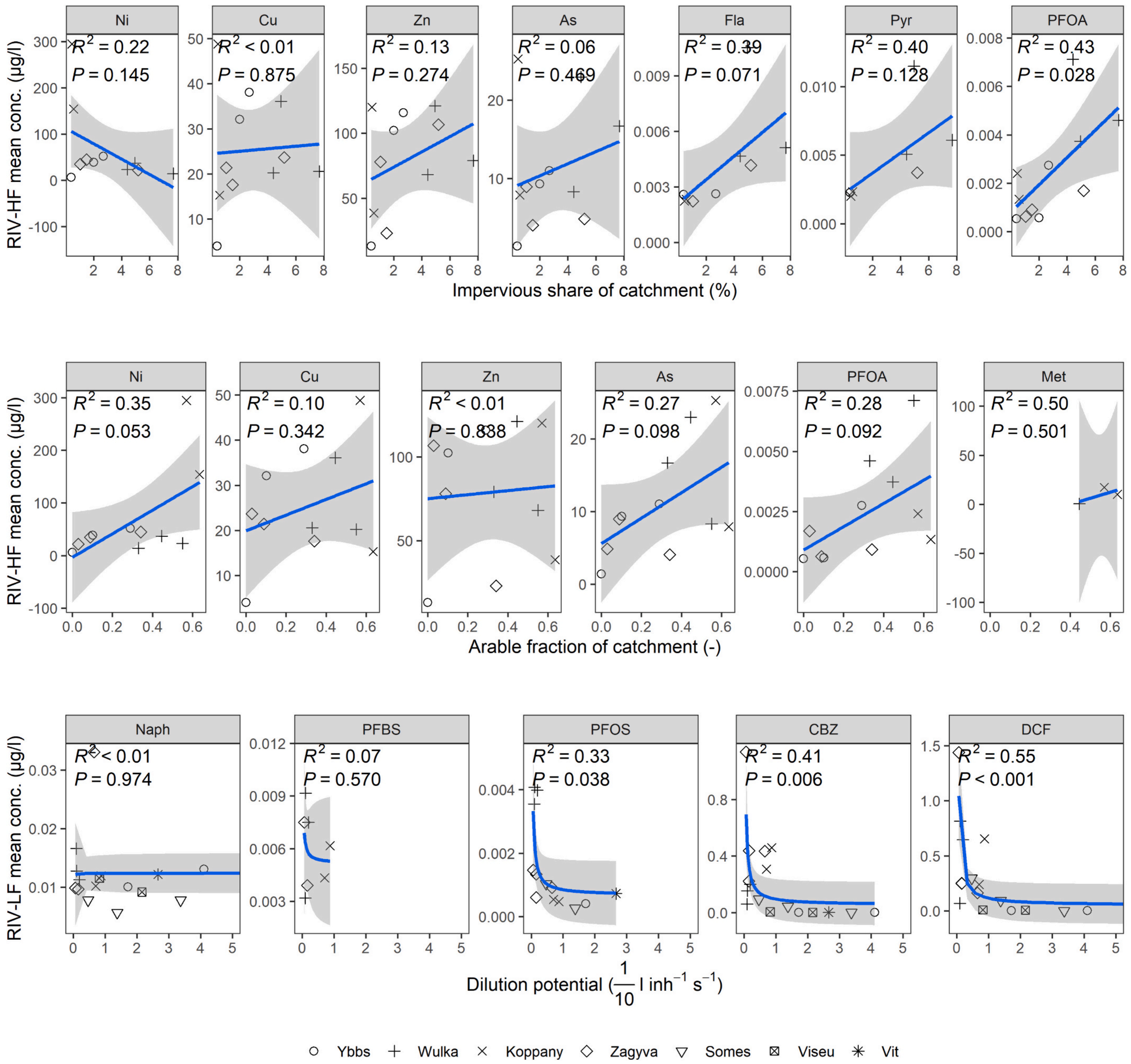

Fig. 6. River high flow mean concentrations versus various catchment properties: the share of impervious areas in the catchment (top row), the share of arable in the catchment (middle row) and the dilution potential, defined as the long-term mean river flow per the number of inhabitants in the catchment (bottom row). The three sub-catchments with >2 l/s/inh ("BVB", "BVC" and "AYH") are not shown on the figure, but their data, if over LOQ, was included in the calculation of R^2 and *P* values. Ni, Cu, Zn, As: heavy metals. Fla: Fluoranthene, Pyr: Pyrene, PFOA: perfluorooctanoic acid, Met: metolachlor; Naph: Naphtalene, PFBS: Perfluorobutane sulfonate, PFOS: Perfluorooctane sulfonate, CBZ: carbamazepine, DCF: diclofenac. R^2: coefficient of determination; P: *p*-value of statistic.

extrapolation in modeling exercises Total heavy metals are strongly associated with small particles suspended in rivers; their adequate quantification requires targeted sampling of river flood events. In addition, they are highly variable in space due to different geogenic conditions. Furthermore, they can originate from various anthropogenic diffuse and point sources in addition to diffuse geogenic sources, making their modeling complex and data intensive. Different PAH forms behave differently and only a few of them could be effectively quantified in the current project, namely the two intermediate forms Fla and Pyr. These are thought to originate from urban diffuse sources. For their effective modeling, WWTP and CSO effluent concentrations and discharge values need to be adequately quantified. The two successfully monitored PFAS forms, PFOA and PFOS, behave rather differently. Firstly, both appear to be ubiquitous, but with higher concentrations in north-western countries than in south-eastern countries. In addition, our research suggests that while both are associated with urban areas, PFOA becomes more concentrated during high flow events, while PFOS remains unchanged. So PFOA tends to be more adsorbed to particles. For widely used pharmaceuticals such as DCF and CBZ, population and consumption data (alternatively: market sales) are essential for adequate modeling (provided that quaternary treatment at WWTP is negligible). Relating population to discharge points, combined with river flow data, can provide reliable assumptions on the riverine concentration of pharmaceutical residues. (Seller et al., 2023; Varga et al., 2023). According to our findings, population data is also effective in predicting river PFOS concentrations, this, however, needs further investigations (Fig. 7).

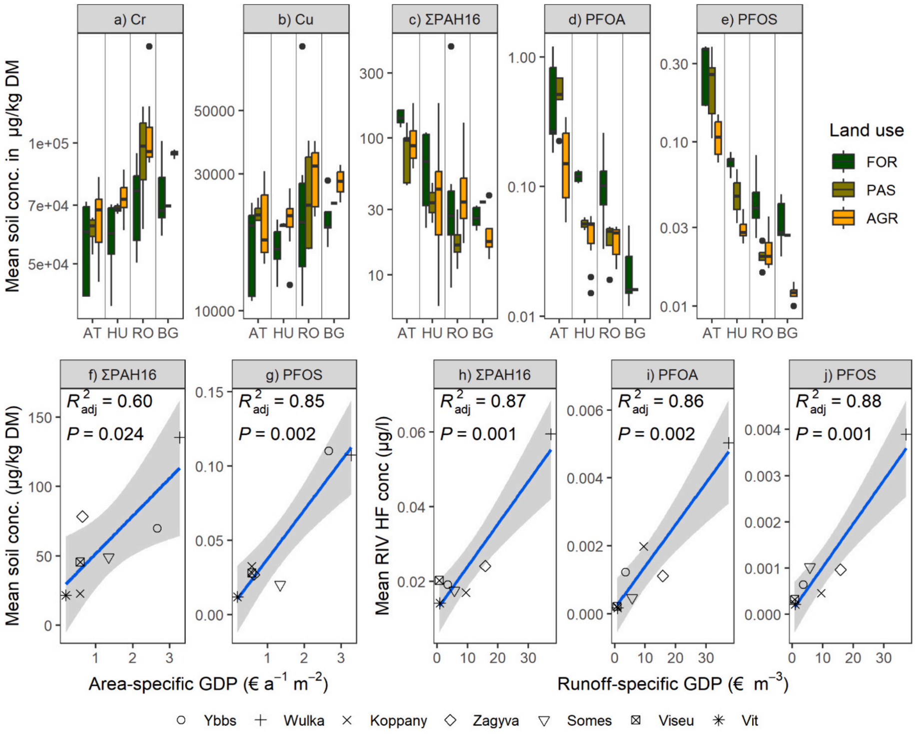

Fig. 7. a-e: Concentration of PTE, PAH and PFAS in forest, pasture and agricultural soils across the countries. f-g: Mean concentration in agricultural soil samples vs area-specific GDP (per capita annual GDP multiplied by the number of inhabitants on the PA, divided by PA area). h-j: Mean river high flow concentration at the PA outflow station vs runoff-specific GDP (per capita annual GDP multiplied by the number of inhabitants on the PA, divided by yearly water runoff).

4. Conclusions

This study presents the lessons learned and results of a concerted and harmonised monitoring programme designed to provide information on the main emission pathways of surface water pollution of hazardous substances across heterogeneous geographical areas of a large river basin. Furthermore, insights are provided into the different patterns of transport of contaminants in rivers. Given the substantial financial resources required for the chemical analysis of hazardous substances at very low concentration levels, we developed a targeted and optimised design comprising stratified composite sampling approaches and including selected substances, which serve as indicators for specific patterns of emission pathways and of environmental fate.

A number of substances exhibit a spatial variation, with the Viseu mining area exhibiting concentrations of most heavy metals that are 2–3 orders of magnitude higher than the surrounding area. In the Carpathian basin, elevated concentrations of geogenic arsenic were detected. It was found that patterns that hold for most PTE should not be used in the case of dissolved arsenic, as arsenic is almost exclusively of natural origin and is primarily conveyed in particulate form through atmospheric transport and surface runoff, and in dissolved form through subsurface flow. The concentration of PFAS in soils decreased from northwestern to southeastern countries by one order of magnitude. Pesticide concentrations were only detected in catchments with a predominantly agricultural land use, with high variability. In particular, pesticides were only detected in rivers where agricultural land use was dominant in the catchment area. The raw pesticide forms indicated a high intra-stational and temporal variance, but the metabolites were more balanced throughout seasons and flow conditions. The specific emissions of the two pharmaceuticals under investigation differed from one another. While the range of 0.7–1.0 mg/cap/day for diclofenac covered all the plants investigated, the values for carbamazepine were more variable, ranging from 0.1 to 1.0 mg/cap/day. Higher concentrations were observed in Hungary and lower ones in Austria. In addition to the regional variations, the type of land use also proved to be an important factor in the variability of the concentration of PTE, PAH, and PFAS in soils.

The differences between river high-flow and low-flow situations were found to be significant for a number of substances. While potentially toxic elements (heavy metals) and pesticides indicated 10 to 200 times higher concentrations during high flow events compared to low flow periods, substances originating from permanent point-source discharges such as the outlet of municipal or industrial wastewater treatment plants were diluted during flood events. While for some chemicals population data and hydrology may be sufficient for predicting in-stream concentrations, the industrial chemicals require detailed knowledge of industrial activities and emissions.

The implementation of a harmonised monitoring programme across different regions of the basin enabled the identification of gradients of water pollution associated with varying economic developments. For instance, the concentrations of PAHs and PFASs in soils decline from Austria through Hungary and Romania to Bulgaria. This suggests that areas with lower economic potential emit less PAHs and PFASs. Conversely, numerous PTE exhibited a contrasting geographical pattern, with elevated concentration levels observed in downstream territories.

The findings of this study underscore the imperative for the implementation of harmonised and coordinated hazardous substance monitoring programs that encompass a wide array of substances, emission sources, pathways, and geographical regions, which is crucial for the reliable development of emission factors.

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CRediT authorship contribution statement

Máté Krisztián Kardos: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Adrienne Clement:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Zsolt Jolánkai:** Writing – original draft, Investigation, Data curation, Conceptualization. **Matthias Zessner:** Writing – review & editing, Funding acquisition, Conceptualization. **Steffen Kittlaus:** Writing – review & editing, Software, Methodology, Investigation, Data curation. **Nikolaus Weber:** Investigation, Data curation. **Oliver Gabriel:** Writing – review & editing, Investigation, Data curation. **Marianne Bertine Broer:** Investigation, Data curation. **Florentina Soare:** Investigation, Data curation. **Carmen Hamchevici:** Investigation, Data curation. **Mugurel Sidau:** Data curation. **Radoslav Tonev:** Investigation, Data curation. **Radmila Milačič:** Writing – review & editing, Resources, Data curation. **Janez Ščančar:** Resources. **Milena Horvat:** Resources. **Katarina Marković:** Resources. **Sandra Kulcsar:** Resources. **Andrea Schuhmann:** Resources. **Gábor Bordós:** Resources. **Eszter Pataj:** Resources. **Ottavia Zoboli:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Lab analysis results are included in (Kittlaus et al., 2023) and are freely downloadable.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174760.

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