Interreg
Danube Region

Co-funded by
the European Union

Tethys

Output 1.7

Harmonized and cost-efficient monitoring strategies as a basis for HS emissions and pollution inventories

Activity leader

Radmila Milačič Ščančar

Authors

Radmila Milačič Ščančar, Janez Ščančar, Miroslav Štrbac (JSI; Jožef Stefan Institute, Slovenia)

Ottavia Zoboli, Meiqi Liu, Matthias Zessner, Nikolaus Weber, Ernis Saracevic (TU Wien, Austria)

Zsolt Jolánkai, Kardos Máté Krisztián, Ildikó Musa, Adrienne Clement (BME; Budapest University of Technology and Economics, Hungary)

Michal Kirchner (WRI; Water Research Institute, Slovakia)

Ioana Nedelea, Constanta Moldovan (NARW; National Administration „Romanian Waters”, Romania)

Radoslav Tonew, Dimitar Mihalkov, Teodora Pakuleva (BWA; Bulgarian Water Association, Bulgaria)

Đorđa Medić, Jasmina Antolić (HV; Croatian Waters, Croatia)

Olha Ukhan, Nataliia Osadcha (UHMI; Ukrainian Hydrometeorological Institute State Service on Emergencies and National Academy of Science, Ukraine)

Marko Marjanović (JCWI; Jaroslav Černi Water Institute, Serbia)

Bojana Knežević, Vladimir Živković, Dijana Đurović, Danijela Šuković (CETI; Center for Ecotoxicological Research Podgorica, Montenegro)

Jelena Vićanović, Aleksandra Kovačević (JUVS; Public Institution “Vode Srpske”, Bosnia and Herzegovina)

Oliver Gabriel, Marianne Bertine Broer (UBA; Environment Agency Austria, Austria)

Table of content

Abstract

Effective management of water pollution is constrained by major knowledge gaps and limited monitoring coverage. To support comprehensive emission inventories and targeted mitigation, emission and water quality models such as MoRE are essential, though they require extensive input data that are often unavailable, especially in non-EU countries. Building on previous initiatives, the Tethys project conducted a pilot action to design and demonstrate fit-for-purpose, cost-efficient monitoring strategies focused on largely unmonitored compartments and emission pathways, including stormwater overflows. A one-year harmonized monitoring campaign across 11 EU and non-EU countries in the Danube River Basin demonstrated the feasibility and value of cost-efficient, basin-wide monitoring strategies. The collected data significantly reduce information gaps and provide a significantly improved basis for the implementation and validation of the MoRE emission model and for comparing contamination levels and substance profiles across countries and water compartments. Results show that metal concentrations in river waters generally comply with WFD environmental quality standards, with exceedances mainly at known industrial, mining, and municipal hotspots. Median metal concentrations were comparable to previous studies, while elevated maxima highlight the strong influence of localized pollution sources. Wastewater treatment was found to be largely effective for metals, whereas untreated discharges led to clear degradation of surface and groundwater quality. Monitoring of PFAS and pharmaceuticals revealed strong spatial and compartment-specific variability, with stormwater and wastewater identified as major emission pathways, while groundwater was mostly unaffected. Overall, the findings confirm the importance of targeted, harmonized monitoring and effective wastewater and runoff treatment to support emission inventories and protect water quality.

This document summarizes the conceptual framework, methodologies, and obtained results, providing guidance for the design and implementation of similar monitoring and inventory efforts in other river basins.

1 Motivation and objectives

Effective control and reduction of water pollution are hindered by severe gaps of knowledge and by lack of robust system understanding. To better assess the extent of surface water pollution beyond the limited number of locations included in national monitoring programmes, and to identify effective mitigation measures, it is necessary to understand and quantify the contribution of different emission pathways at catchment and national scales. In this context, emission and water quality models are essential instruments to identify the most relevant emission pathways for different types of contaminants, to describe how pollution is distributed across large river basins, and to allocate in a targeted way resources for more in-depth investigations. Multiple models have been developed to address these questions, each of them with its own strengths and weaknesses as well as a different level of complexity and data requirements. The Tethys project focuses on the implementation of the MoRE model at transnational and national levels. This tool is designed to apply the pathway-oriented approach set out in the third tier of the modelling framework for establishing emission inventories of priority substances, as detailed in the WFD CIS Guidance Document No. 28 (EU, 2012). This model has been shown to outperform simpler modelling approaches in estimating concentrations and loads of trace contaminants in unmonitored surface waters (Kittlaus et al, 2022). Nevertheless, it requires extensive and robust input data on the occurrence and concentration levels of trace contaminants in multiple environmental and engineered compartments, which in many cases is still hardly available in the needed amount and quality.

The Interreg Danube Transnational Programme project, Danube Hazard m^{3}c presented and demonstrated in several pilot regions innovative monitoring approaches and, through a series of national training workshops, enhanced institutional capacity via a series of national training sessions in multiple Danube countries. Nevertheless, new solutions and capacity building are required that go beyond the scope of the Danube Hazard m^{3}c project. For example, there is a need to focus on largely unmonitored compartments and emission pathways, such as stormwater overflows, to identify unknown hotspots of per- and polyfluoroalkyl substances and of other legacy pollutants, and to address the serious deficiencies and gaps in data availability identified especially in non-EU countries.

In such context, within the Tethys project we carried out a pilot action to test and demonstrate how to design and carry out a fit-for-purpose and cost-efficient monitoring as a basis for hazardous substances (HS) emissions and pollution inventories. This pilot action was mostly dedicated to non-EU countries, but it also included a focus on emission pathways from environmental and urban compartments which are still largely unmonitored and yet are recognized as emerging critical emissions loads of HS in both EU and non-EU countries. The conceptual framework, methodologies applied and details on the monitoring campaign carried out in each country are described in the Output 1.1 of the Tethys project. This document draws on the lessons learned during the pilot action, but also on previous related research activities, and provides a compact summary of the design of monitoring campaigns aiming at supporting the application and validation of emission models and more in general at establishing emission inventories. The approaches and methods described can be used as guidance for similar endeavours in other river basins as well. In addition, the results of the monitoring carried out in the pilot action are described and discussed in the context of their usefulness for the 3establishment of emission inventories.

2 Selection of contaminants

When designing and implementing monitoring, it is essentials to carefully consider and select the scope of compounds to analyse, in addition to questions concerning the sampling frequency and the sampled medium or matrix. The Water Framework Directive and related European and national legislation define prioritisation criteria and set out rules and criteria to select for which contaminants emission inventories are to be established. Further, there might be compelling reasons to expand the scope of contaminants in the emission inventories, especially in the context of pollution control and management in a large transnational river basin such as the Danube River Basin. The selection and prioritisation of contaminants for such endeavour over the past years has become increasingly important but also highly challenging. This is because there are already over 350,000 chemicals and chemical mixtures registered for production and use worldwide (Wang et al., 2020). Weisner et al. (2022) highlighted a crucial issue in the context of pesticides: official monitoring in Europe is currently severely underestimating actual pollution levels and impact due, among other weaknesses of the monitoring approaches, to outdated lists of regulated substances including mainly legacy and banned substances no longer used in agriculture. Similar issues also apply to other chemicals being replaced by the industry with substitute compounds. Due to the abovementioned reasons, a revision of the list of priority substances at EU level is ongoing. However, it is evident that even the proposed revised list is affected by considerable limitations in the face of the overwhelming number of compounds being released into the environment. When it comes to emission control and designing programmes to mitigate trace contaminants, it is clear that monitoring the full spectrum is unrealistic. A promising approach might instead rely on selecting and focusing on specific trace contaminants, which are representatives of different sources, emission pathways and environmental behaviours and can thus serve as indicators for the effectiveness of mitigation measures for larger groups of compounds with similar characteristics and environmental fate.

Once the list of contaminants is defined, it is crucial to identify the environmental and engineered compartments in which they occur and the sources and pathways from which they are released and transported into water bodies, in order to optimise and allocate more effectively the resources required for monitoring. Moreover, there are other crucial aspects to be considered. Different groups of organic and inorganic trace contaminants have different requirements regarding the necessary water volume, need of analysing sediments or biota in addition or in alternative to water, adequate vessel and sampling materials, the maximum time-lag between sampling and analysis, or the need for the immediate addition of stabilising chemicals.

3 Description of relevant compartments, catchment types and sampling frequency to support or validate emission models

Substance-specific data appropriate for applying and validating emission models at the national or transnational level are generally spatially and temporally scarce. An exception is metals, which are generally spatially and temporally better monitored than organic trace contaminants, for example in the Transnational Monitoring Network (TNMN) but also in the larger network of monitoring stations at national level.

The most critical substance-specific data gaps for applying and validating a pathway-oriented emission model such as the MoRE model, on which the Tethys project focused by sampling across the Danube River Basin (DRB) involved the following environmental and engineered compartments:

- Major rivers and tributaries to support model validation.
- Rivers at locations that can enhance input data and validation for specific emission pathways.
- Rivers at background locations.
- Specific compartments relevant to emission pathways, such as wastewater treatment plant (WWTP) effluents, groundwater and urban storm runoff water.

The sampling locations within the Tethys project were selected according to the following criteria, which can be recommended as general guidance applicable to establish transnational emission inventories in other basins as well:

- The Danube River was sampled near national borders, as many industrial and pharmaceutical substances are closely associated with demographic factors.
- At TNMN stations, samples were collected for the analysis of PFAS and pharmaceuticals, which are not included in the regular TNMN monitoring programme.
- As national datasets for metals are already comprehensive, alternative sites were selected for metals, including hotspots such as mining areas, metal works, chemical industry and landfills.
- Given the spatial scarcity of WWTP data in the eastern–southern part of the DRB, priority was given to sampling as many WWTP outflows as possible. In areas without a WWTP, direct municipal or industrial discharges into the river were sampled.
- The site selection was partially substance-specific. Sampling sites for the analysis of PFAS in samples were chosen based on potential sources of PFAS pollution, such as the use of firefighting foams at airports, and activities in the textile, paper, or sanitary industries. In contrast, sampling sites for the analysis of pharmaceuticals in samples were selected near municipal WWTP effluents, effluents from pharmaceutical manufacturing facilities or landfills. For stormwater runoff, a key pathway for many substances, samples were collected from larger urban catchments.
- In each region, river water samples were also collected from background locations, pristine areas with no known anthropogenic pressures besides atmospheric transport and deposition.
- All sampling sites were located close to river water gauging station equipped with discharge-water level (Q–H) rating curves or continuous flow measurements.

3.1 Selection of sampling sites in non-EU countries

As in the Danube River Basin the largest substance-specific gaps of data and information were identified in non-EU countries, the Tethys project concentrated its monitoring efforts in Montenegro, Bosnia and Herzegovina, Serbia and Ukraine. In those countries, extensive sampling campaigns were carried out over one year focusing on river water, wastewater, and groundwater.

As outlined in the Output 1.1, the criteria for the selection of the sampling sites were jointly defined by the whole partnership, but each partner was responsible for proposing and selecting sampling sites in its national territory to ensure that samples represented the most relevant pollution sources or lack thereof in case of background catchments.

3.1.1 River sampling

River water was collected from rivers and/or their tributaries for model validation and source identification, covering:

1. Outflow points of major tributaries or important cross-sections of the Danube for load validation.
2. Potentially polluted sites (hot spots) and locations where specific pollution sources were expected, for source identification.
3. Background locations.

Under base-flow conditions (low to mid-flow), four samples were taken at each sampling location (one every three months).

Under high-flow conditions, two samples were taken at selected locations.

In total, 50–70 river water samples were collected per country.

3.1.2 Wastewater sampling

Wastewater sampling was conducted at the effluent of industrial, municipal, or industrial-municipal WWTPs, and/or at treated wastewater discharge points from mining areas. A total of 6–12 sampling sites per country were selected to represent characteristic pollution points.

At each site, three effluent samples were collected over one year.

Where no WWTP was available, untreated wastewater was collected at the point of discharge into the river.

In total, 18–36 wastewater samples were collected per country.

3.1.3 Groundwater sampling

Groundwater sampling was performed at 2–4 specific sites representing characteristic pollution points (e.g., groundwater near landfills or airports).

At each site, two groundwater samples were collected over one year.

In total, 4–8 groundwater samples were collected per country.

Overall, the total number of samples (river water, wastewater, and groundwater) in non-EU countries was up to 100.

3.2 Selection of sampling sites in EU Countries

In EU countries (Austria, Slovakia, Slovenia, Bulgaria, Romania, Croatia, and Hungary), targeted sampling campaigns were conducted focusing on river water, wastewater, and/or urban stormwater runoff, based on the identified most crucial gaps of substance-specific information and data for the MoRE model application and validation at transnational level for the whole Danube River Basin.

As outlined in the Output 1.1, the criteria for the selection of the sampling sites were jointly defined by the whole partnership, but each partner was responsible for proposing and selecting sampling sites in its national territory to ensure that samples represented the most relevant pollution sources or lack thereof in case of background catchments.

3.2.1 River Sampling

River water was collected from main rivers and/or their tributaries for model validation and source identification, covering:

1. Outflow points of major tributaries or important cross-sections of the Danube for load validation.
2. Potentially polluted sites (hot spots) and locations where specific pollution sources were expected.
3. Background locations.

Samples were taken under base-flow conditions (low to mid-flow). At each sampling location, four samples were collected (one every three months).

In total, 8–12 river water samples were collected per country.

3.2.2 Wastewater Sampling

Wastewater was sampled at the effluent of industrial, municipal, or industrial-municipal WWTPs and/or at treated wastewater discharge points from mining areas. A total of 3–5 sampling sites per country were selected to represent characteristic pollution points.

In total, 9–15 wastewater samples were collected per country.

3.2.3 Urban stormwater runoff sampling

In countries where sampling of urban stormwater runoff from roads was possible due to available equipment (Austria and Hungary), samples were collected at 3–8 locations, at least three times per year at each location.

In total, 9–24 stormwater runoff samples were collected per country.

The total number of samples (river water, wastewater, and urban stormwater runoff) in EU countries was up to 25.

4 Benefit and need of online monitoring stations and of integrated composite samples

The Tethys project included exclusively monitoring approaches based on grab samples, owing to the focus being on the strategic design and selection of compartments, locations and frequency of sampling, as well as due to budgetary and organisational constraints. Nevertheless, the Danube Hazard m^{3}c project previously demonstrated the great benefit and advantages of integrating within national monitoring programmes also the collection of time or space integrated composite samples and of including a selected number of online monitoring stations, especially for the purpose of robustly estimating annual riverine loads.

The main drawback of grab samples is that they provide only a snapshot of water quality conditions at a specific location and time. In the event of pronounced dynamic variations in concentration, these will not be sufficiently and robustly represented by low-frequency grab samples. By deploying automatic samplers that can be controlled remotely and programmed to activate according to changing water levels or e.g. turbidity, the frequency of grab sampling can be increased and adjusted in order to cover dynamic changes in water quality in a representative manner. If automatic samplers are used to generate integrated composite samples over time, the total costs for chemical analyses does not necessarily have to raise while the representativeness of the samples significantly increases. There are two fundamental ways in which composite sampling can be configured: time-proportional or flow-proportional integration. Whereas the set up and operation of time-proportional sampling is relatively simple, flow-proportional sampling is technically more demanding and challenging, especially in small, highly dynamic streams.

Whether it is adequate and necessary to collect time- or flow-proportional composite samples instead of grab samples depends on multiple factors. These include the sources and environmental transport behaviour of the specific contaminants, the characteristics of the catchments (e.g. the presence or absence of municipal and industrial wastewater treatment plants), and the purpose of the monitoring.

5 Recommendations for methodology of sampling, transport, storage and analyses

Sampling, sample storage, and sample transport depend on both the sample matrix and the substance to be measured. Samples must be collected in pre-cleaned bottles, as described in the SOP (Tethys deliverable D1.1.1, 2024). When collecting water samples for metal analysis, powderless nitrile gloves should be worn throughout the entire sampling process. Sampling bottles, bottle caps, and other equipment must never be placed on the ground. If PFAS and/or pharmaceutical sampling is conducted simultaneously with metal sampling, PFAS and pharmaceutical samples must be collected first. All necessary steps to prevent contamination during sampling should be strictly followed, as detailed in SOP D1.1.1 (2024).

Blanks arising from the sampling procedures (bottles, filters, acids), are evaluated for individual class contaminants by the laboratories performing the analysis. If the instructions how to perform sampling is strictly considered, contamination is avoided and blanks are negligible.

To reduce the possibility of contamination and to unify the sampling protocol, the same bottles and chemicals for sample preservation are recommended to be used across the catchments investigated.

5.1 River water sampling procedure

River water sampling is performed by collecting grab samples from the main stream of the river, either from a ship or from a bridge. When approaching the sampling point by ship, the vessel speed must be reduced to minimize disturbance of the water.

Water samples are collected from the bow of the ship, facing upstream, using a sampling extension rod with a container. The sampling container should be submerged approximately 30 cm below the water surface (ISO 5667-3, 2018). Care must be taken to avoid contact between the container or water and any part of the boat or clothing. Rinse the container three times with river water before collecting the sample. After sampling, seal the container with a cap and label it with all necessary information.

Samples must be preserved and stored according to the guidelines specified for each contaminant class, described in SOP D1.1.1 (2025). Ensure that appropriate and clean sampling containers are used for each contaminant type.

Important Notes:

- Fill bottles to a maximum of 95% of their volume.
- Samples must be transported to the laboratory under cooled conditions within 4 hours of collection for freezing or refrigeration, depending on the storage requirements of the contaminant class.

Safety Warnings:

- When entering the river to reach the boat, be aware of possible hazards such as soft mud, quicksand, deep holes, and swift currents.
- Attach a safety line to a secure object on the riverbank for support.
- The use of life jackets is strongly recommended.
- River sampling should always be conducted by at least two people working together.

5.1.1 Required sample volumes, bottles and sample preservation for river water sampling

Table 1 provides details on the required sample volumes, types of sampling containers, and preservation procedures for river water samples for different contaminant classes.

Table 1: Sample volumes, bottles, and preservation procedures for river water samples.

Parameter	**Sampling container and volume**	**Sample type, volume and bottle material**	**Sample preservation procedure**
Metals – Total metal content	250 mL PE	Acidified whole water sample	Add 0.375 mL of HNO_3 (suprapure) immediately after sampling to 250 mL of whole water sample (final pH < 2)
Metals – Dissolved metal content	50 mL PE	Filtered and acidified water sample	Filter the whole water sample directly into a 50 mL PE bottle using a 0.45 µm membrane filter, then add 0.075 mL of HNO_3 (suprapure) immediately after sampling (final pH < 2)
PFAS and Pharmaceuticals	1 L HDPE	1 L water sample	No chemical preservation required

5.2 Wastewater sampling procedure

Effluent from municipal and industrial wastewater treatment plants (WWTPs) is collected as a weekly composite sample during dry weather conditions. Depending on the equipment available at the WWTP, two procedures can be followed:

Option 1: WWTP equipped with an autosampler and flow measurement device

Seven daily composite samples (24-hour mixed samples collected each day) are combined into a flow-proportional weekly composite sample.

Option 2: WWTP not equipped with an autosampler

Seven grab samples collected each day at the same time are combined into a time-proportional weekly composite sample.

Option 1 is preferred. When autosamplers are regularly in use, any PFAS from materials will have been washed out. Blanks must be checked whenever new autosamplers are employed.

5.2.1 Required sample volumes, bottles and sample preservation for wastewater sampling

Table 2 provides details on the required sample volumes, types of sampling containers, and preservation procedures for wastewater samples for different contaminant classes.

Table 2: Sample volumes, bottles, and preservation procedures for wastewater effluent weekly composite samples.

Parameter	**Sampling container**	**Sample type, volume and bottle material**	**Sample preservation procedure**
Metals	1 L PE	Acidified wastewater sample. Fill with 700 mL of the flow-proportional or time-proportional weekly composite sample	Option 1: Add 0.15 mL of HNO_3 (suprapure) to 100 mL of each daily composite sample (7 daily composites form 0.7 L of flow-proportional weekly composite sample) Option 2: Add 0.15 mL of HNO_3 (suprapure) to 100 mL of each daily grab sample (7 daily grab samples form 0.7 L of time-proportional weekly composite sample)
PFAS and pharmaceuticals	1 L HDPE (both PFAS and pharmaceuticals together)	Wastewater samples filled with 1 L of the flow-proportional or time-proportional weekly composite sample	Option 1: Collect 0.5 or 1 L per day depending on equipment (7 daily composites form ~0.98 L of flow-proportional weekly composite sample) Option 2: Collect 0.14 L per day (7 daily grab samples form ~0.98 L of time-proportional weekly composite sample). No chemical preservation required

5.3 Groundwater sampling procedure

Groundwater samples should be collected from pumping stations equipped with taps. Before taking a sample, it is essential to flush the pipes to ensure that stagnant water is removed. Typically, a minimum of 100 l of water should be allowed to flow through the pipes and be discarded before collecting the sample for analysis.

5.3.1 Required sample volumes, bottles and sample preservation for groundwater sampling

Table 3 provides details on the required sample volumes, types of sampling containers, and preservation procedures for wastewater samples for different contaminant classes.

Table 3: Sample volumes, bottles, and preservation procedures for groundwater samples.

Parameter	Sampling container	Sample type, volume and bottle material	Sample preservation
Metals – Dissolved metal content	50 mL PE	Filtered and acidified water sample. Filter the whole water sample through a 0.45 µm membrane filter directly into a 50 mL PE bottle	Add 0.075 mL of HNO_3 (suprapure) immediately after sampling (pH<2)
PFAS and pharmaceuticals	1 L HDPE for both PFAS and pharmaceuticals	1 L water sample in a single bottle.	No chemical preservation required

5.4 Urban stormwater runoff sampling procedure

Stormwater runoff from urban areas should ideally be collected at locations where an automatic sampler and sensors for measuring water level or discharge are available. In such cases, discharge-proportional event samples should be collected and delivered for analysis.

If an automatic sampler is not available, grab samples should be taken to cover the entire rainfall event, with particular attention to the first flush, which is especially important. By installing sensors to monitor changes in water level during the event, discharge-proportional composite samples for each event can later be formed from the grab samples.

Alternatively, fewer events can be sampled, with individual samples collected during these events analysed separately to provide a deeper understanding of contaminant transport dynamics.

5.4.1 Required sample volumes, bottles and sample preservation for urban stormwater runoff sampling

Table 4 provides details on the required sample volumes, types of sampling containers, and preservation procedures for wastewater samples for different contaminant classes.

Table 4: Sample volumes, bottles, and preservation procedures for urban stormwater runoff samples.

Parameter	Sampling container	Sample type, volume and bottle material	Sample preservation
Metals – Total metal content	250 mL PE	Acidified whole water sample	Add 0.375 mL of HNO_3 (suprapure) immediately after sampling to 250 mL of whole water sample (final pH < 2)
PFAS and pharmaceuticals	1 L HDPE for both PFAS and pharmaceuticals	1 L water sample in a single bottle	No chemical preservation required

5.5 Storage and sample transport

5.5.1 Metals

Before storing the samples, cover the sample labels with wide transparent tape to prevent them from being erased during freezing. Frozen samples are kept at −20 °C until analysis or transport to the receiving laboratory. The samples are transported by express courier (within 48 hours) in polystyrene foam boxes filled with dry ice or equipped with cooling pads. The receiving laboratory performs the analysis immediately upon receipt.

5.5.2 PFAS and pharmaceuticals

After sampling, store the samples under cooled conditions at a temperature below 6 °C. The cooled samples are kept this way until analysis or transport to the receiving laboratory. The samples are transported by express courier (within 48 hours) in boxes covered with jute, using cooling pads to maintain cool conditions. The receiving laboratory performs the analysis no later than seven days after sampling.

5.6 Analyses of HS

The analyses of HS follow the procedures described in detail in the Tethys Output document O1.1 (2025).

6 Results of chemical analyses

Metals, and PFAS and pharmaceuticals were quantified in four types of water samples: river water, wastewater, groundwater, and urban stormwater runoff samples. In river water, both total and dissolved metal concentrations were measured. In wastewater and urban stormwater runoff samples, total metal concentrations were determined, whereas in groundwater, only dissolved metal concentrations were analysed. PFAS and pharmaceutical concentrations were performed from whole water samples.

6.1 Results of metal analyses

6.1.1 Metal concentrations in river water samples

In order to support the understanding of element transport in river water and for modelling purposes, both total and dissolved metal concentrations were measured, although the Water Framework Directive (WFD) (Directive 2000/60/EC) and its Daughter Directives (Environmental Quality Standards 272/2009; Directive 2013/39/EU) establish environmental quality standards (EQS) only for dissolved metal concentrations in surface waters (Table 5).

With regard to Ni and Pb, Directive 2013/39/EU (which amends Directives 2000/60/EC and 2008/105/EC concerning Priority Substances in Water Policy) reduced the EQS values compared to the Directive 2000/60/EC: the EQS for dissolved Ni content was lowered from 20 ng/L to 4 ng/L, and for Pb from 7.2 ng/L to 1.2 ng/L, with the EQS now referring to bioavailable concentrations of Ni and Pb.

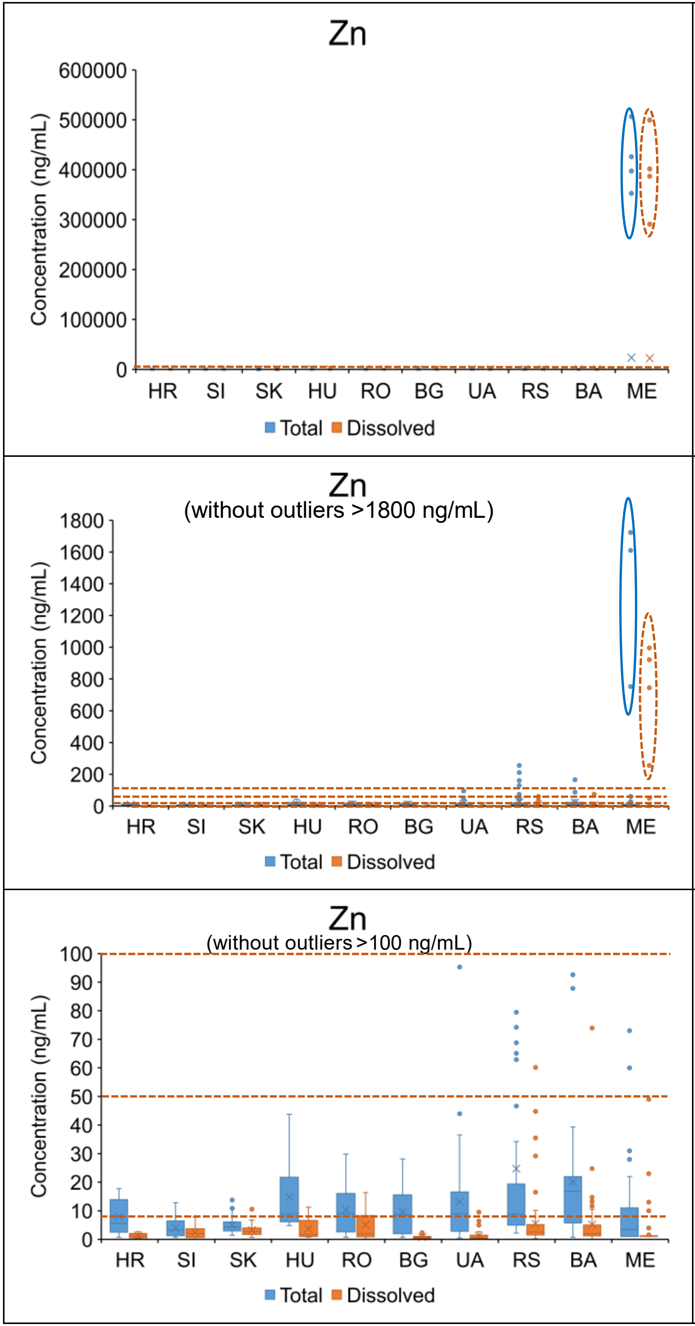
Table 5: EQS for dissolved metal concentrations.

Metal	**EQS**	
	Directive 2013/39/EU – Priority Hazardous Substances	Environmental Objectives 272/2009 – Specific Pollutants
Cd	<40 mg/L $CaCO_3$……………………….≤0.08 ng/mL 40–50 mg/L $CaCO_3$ …………………..0.08 ng/mL 50–100 mg/L $CaCO_3$ …………………0.09 ng/mL 100–200 mg/L $CaCO_3$…………………0.15 ng/mL ≥100 mg/L $CaCO_3$ ……………………..0.25 ng/mL	
Pb*	1.2 ng/mL	
Ni*	4 ng/mL	
Cr		Cr(III) 4.7 ng/mL, Cr(VI) 3.4 ng/mL
Zn		≤10 mg/L $CaCO_3$…………………………..8 ng/mL 10–100 mg/L $CaCO_3$ …………………..50 ng/mL >100 mg/L $CaCO_3$ …………………….100 ng/mL
Cu		≤100 mg/L $CaCO_3$)……………………….5 ng/mL >100 mg/L $CaCO_3$ ………………………30 ng/mL
As		25 ng/mL

* These EQS refer to bioavailable concentrations of Ni and Pb

6.1.1.1 Zinc

Total and dissolved Zn concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 1.



Mjedenički Stream (ME) — abandoned zinc and lead mine, rich in sulfide minerals.

Sampling site	Zn (ng/mL)
RIV-MEMP-01T	506690
RIV-MEMP-01D	499520
RIV-MEMP-02T	426020
RIV-MEMP-02D	401690
RIV-MEMP-03T	352743
RIV-MEMP-03D	290898
RIV-MEMP-04T	397510
RIV-MEMP-04D	386774

Mojkovac, Rudnica River (ME) — former lead and zinc ore mining.

Sampling site	Zn (ng/mL)
RIV-MERU-02T	1610
RIV-MERU-02D	922
RIV-MERU-03T	1742
RIV-MERU-03D	996
RIV-MERU-04T	1723
RIV-MERU-04D	255

Foča, Drina River (BA) — municipal influence and rafting activities. Wastewater discharged untreated into the river.

Sampling site	Zn (ng/mL)
RIV-BA-RSFO-02T	165
RIV-BA-RSFO-02D	73,9

Mojsinje, Južna Morava River (RS) — municipal influence, metal and chemical industry. Wastewater discharged mostly untreated into the river.

Sampling site	Zn (ng/mL)
RIV-RSMO-03T	79,4
RIV-RSMO-03D	60,1

EC Environmental Objectives 272/2009 – Specific Pollutants

EQS for Zn with regard to water hardness:
≤10 mg/L $CaCO_3$ (soft)……………………….....8 ng/mL Zn
10–100 mg/L $CaCO_3$ (medium-hard)..........50 ng/mL Zn
>100 mg/L $CaCO_3$ (hard)…………………...100 ng/mL Zn

Figure 1: Total and dissolved Zn concentrations in river water samples from EU and non-EU countries within the DRB.

The data in Figure 1 show that the concentrations of total and dissolved Zn particularly at the two sampling sites in Montenegro: Mjedenički stream and Mojkovac are significantly higher than at other locations.

As far it concerns the Mjedenički stream (Figure 2, left), the area is naturally enriched with sulfide minerals such as galena (PbS), pyrite (FeS_2), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$), where ore mining took place in the past. In the acidic environment of the ore slag, *Acidithiobacillus* bacteria (rodshaped, acidophilic, chemolithotrophic bacteria) developed. Two species are present that contribute to the bioleaching of metals:

Acidithiobacillus thiooxidans oxidizes sulfide minerals, leading to the formation of sulfate (SO_4^{2-}) and protons (H^+), as well as sulfuric acid (H_2SO_4), which lowers pH to around 3–4.

Acidithiobacillus ferrooxidans oxidizes Fe^{2+} to Fe^{3+}. Ferric iron (Fe^{3+}) further attacks sulfide minerals, generating additional H_2SO_4 and releasing metals from the minerals into surface waters.

Acid mine drainage from mine pits, together with microbially mediated bioleaching, contributes to the extremely high levels of total and dissolved metals in the Mjedenički Stream. The concentration of dissolved Zn is practically identical to its total concentration. The EQS value for dissolved Zn in medium-hard water (50 ng/mL) was exceeded by up to 10,000 times.

Figure 2: Highly contaminated river sites in Montenegro. Left: highly contaminated sampling site at the Mjedenički Stream, Montenegro. An abandoned zinc- and lead-mining area affected by bioleaching from Acidithiobacillus bacteria. Right: Contaminated Mojkovac site on the Rudnica River, Montenegro, impacted by former lead and zinc ore mining activities.

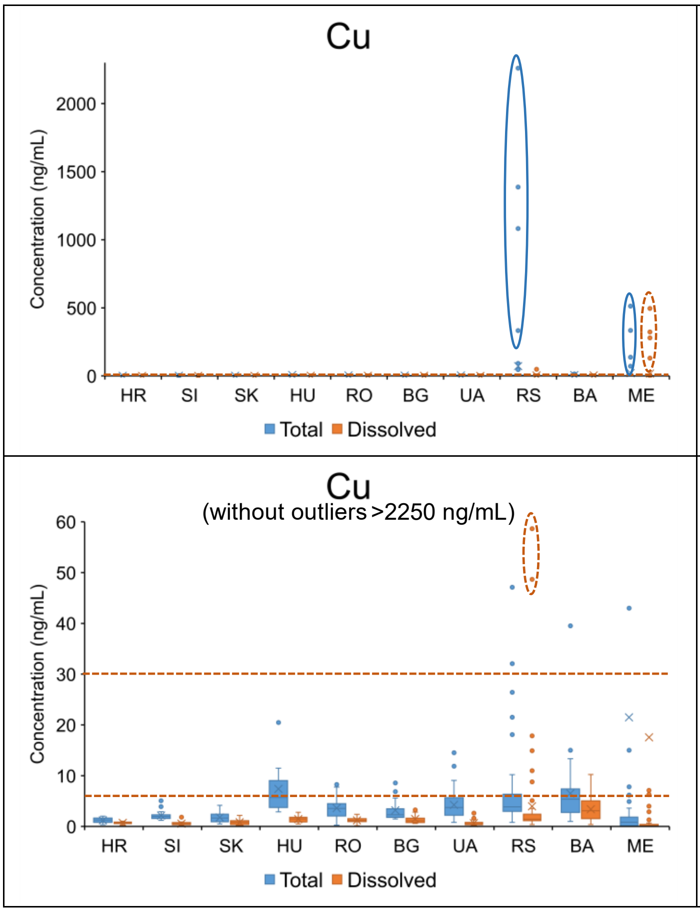
At the Mojkovac site (Figure 2, right), the area is affected by historical lead and zinc ore mining activities. Dissolved Zn represents 15–60% of the total Zn concentration in the Rudnica River water, indicating lower Zn mobility compared to the Mjedenički Stream. The EQS value for dissolved Zn is exceeded by up to 10 times, highlighting a notable environmental concern.

At all other sites investigated, the EQS for Zn (50 ng/mL for medium-hard water) was exceeded only once, at two sampling locations on the Drina and Južna Morava rivers (Figure 3). In the Drina River, at the Foča site in Bosnia and Herzegovina, the river is impacted by the direct discharge of untreated wastewater from municipal source and rafting activities. At the Južna Morava River, at Mojsinje in Serbia, untreated wastewater from municipal, metal, and chemical industry sources is discharged directly into the river.

Figure 3: Foča on the Drina River in Bosnia and Herzegovina (left) and Mojsinje on the Južna Morava River (right), both affected by untreated wastewater from municipal and industrial sources.

6.1.1.2 Copper

Total and dissolved Cu concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 4.



Mjedenički Stream (ME) — abandoned zinc and lead mine, rich in sulfide minerals.

Sampling site	Cu (ng/mL)
RIV-MEMP-01T	334
RIV-MEMP-01D	323
RIV-MEMP-02T	350
RIV-MEMP-02D	280
RIV-MEMP-03T	513
RIV-MEMP-03D	496
RIV-MEMP-04T	138
RIV-MEMP-04D	131

Rogotina, Borska River (RS) — intensive gold and copper mining.

Sampling site	Cu (ng/mL)
RIV-RSBR-01T	2260
RIV-RSBR-01D	14,9
RIV-RSBR-02T	1386
RIV-RSBR-02D	11,0
RIV-RSBR-03T	1082
RIV-RSBR-03D	58,7
RIV-RSBR-04T	332
RIV-RSBR-04D	48,7

EC Environmental Objectives 272/2009 – Specific Pollutants

EQS for Cu with regard to water hardness:

≤100 mg/L $CaCO_3$ (medium-hard).............5 ng/mL Cu
>100 mg/L $CaCO_3$ (hard)..........................30ng/mL Cu

Figure 4: Total and dissolved Cu concentrations in river water samples from EU and non-EU countries within the DRB.

As shown in Figure 4, very high concentrations of Cu were measured in the river water of the Mjedenički Stream, Montenegro. Complex physicochemical and microbiological processes lead to the release of Cu from mineral matrices, resulting in concentrations ranging from 140 to 510 ng/mL, with dissolved Cu being practically equal to the total Cu content. The EQS value for dissolved Cu in medium-hard water (5 ng/mL) was exceeded by up to a factor of 100, raising environmental concerns.

Completely different behaviour is shown by the measured Cu concentrations in the Borska River at the Rogotina sampling site in Serbia, an area of intensive gold and copper mining (Figure 5).

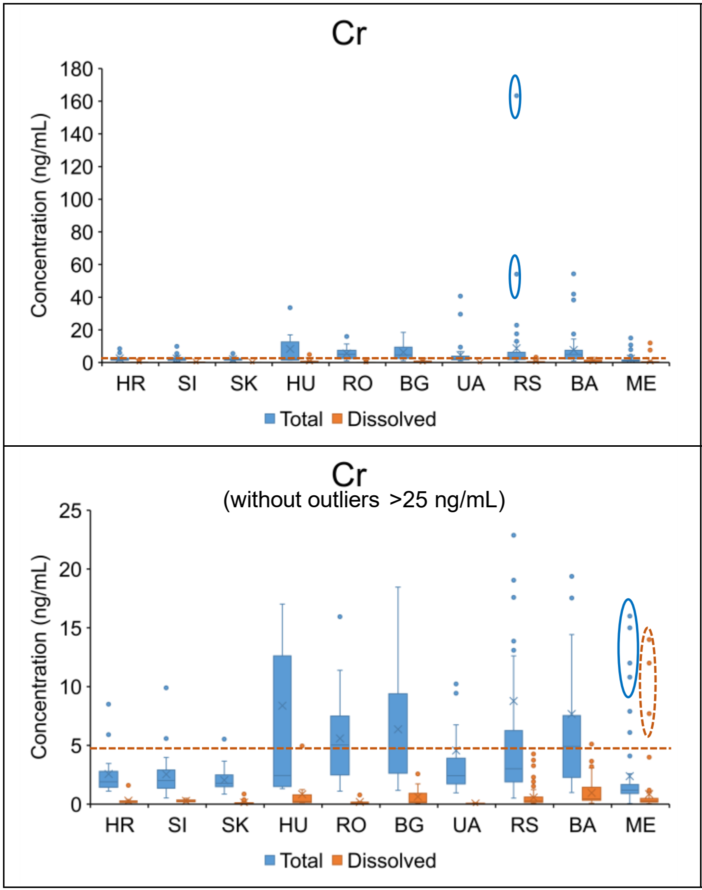
Figure 5: Rogotina on the Borska River in Serbia, impacted by intensive gold and copper mining.

Total Cu concentrations, which are predominantly bound to particulate matter, are very high (ranging from 330 to 2260 ng/mL), while dissolved Cu concentrations represent only 1 to 15% of the Cu total concentration. The EQS for the dissolved fraction of Cu in medium-hard water is exceeded by 2 to 12 times. In addition to environmental concerns due to dissolved Cu, the high concentration of Cu bound to particulate matter may also serve as a source of dissolved Cu.

At other sites investigated, the EQS for Cu in medium-hard water (5 ng/mL) was slightly exceeded twice at the Rudnica River at the Mojkovac site in Montenegro, a former lead and zinc ore mining area. At all other sampling sites across the DRB, the EQS for Cu was not exceeded.

6.1.1.3 Chromium

Total and dissolved Cr concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 6.



Batrage, Ibar River (RS) — the elevated Cr and Ni levels are of natural origin from serpentinite rocks.

Sampling site	Cr (ng/mL)
RIV-RSBA-01T	163
RIV-RSBA-01D	0,270

Rogotina, Borska River (RS) — intensive gold and copper mining.

Sampling site	Cr (ng/mL)
RIV-RSBR-01T	56,0
RIV-RSBR-01D	0,591
RIV-RSBR-02T	54,8
RIV-RSBR-02D	3,75
RIV-RSBR-03T	22,9
RIV-RSBR-03D	0,395

Mjedenički Stream (ME) — abandoned zinc and lead mine, rich in sulfide minerals.

Sampling site	Cr (ng/mL)
RIV-MEMP-01T	10,8
RIV-MEMP-01D	7,7
RIV-MEMP-02T	16,0
RIV-MEMP-02D	14,0
RIV-MEMP-03T	15,0
RIV-MEMP-03D	12,0

EC Environmental Objectives 272/2009 – Specific Pollutants
EQS for Cr:
Cr(III)…………………………………..……. 4.7 ng/mL Cr
Cr(VI)………………………….. ………..…3.4 ng/mL Cr

Figure 6: Total and dissolved Cr concentrations in river water samples from EU and non-EU countries within the DRB.

As shown in Figure 6, high concentrations of total Cr were occasionally determined in the Ibar River at the Batrage sampling site in Serbia, where elevated Cr and Ni levels arise from natural sources in serpentinite rocks. Cr is almost exclusively bound to particulate matter in river water, while the dissolved Cr content represents only 0.2% of its total concentration. A similar behaviour is observed for Cr in the Borska River at the Rogotina site in Serbia (a site with intensive gold and copper mining activities). Total Cr concentrations range from 23 to 56 ng/mL, with the dissolved Cr fraction representing only 1 to 7% of its total content. At both sampling sites, dissolved Cr concentrations did not exceed the EQS value of 4.7 ng/mL Cr(III). It is assumed that Cr in river samples is present in the trivalent oxidation state, as the sampling sites do not indicate sources of hexavalent Cr. The data from Figure 7 further indicate slightly elevated total Cr concentrations 10 to 18 ng/mL in the river water of the Mjedenički Stream, Montenegro. The concentration of dissolved Cr was slightly lower of its total content and exceeded the EQS value by up to a factor of 3. At other sampling sites investigated, the dissolved Cr concentrations were below or close to the EQS.

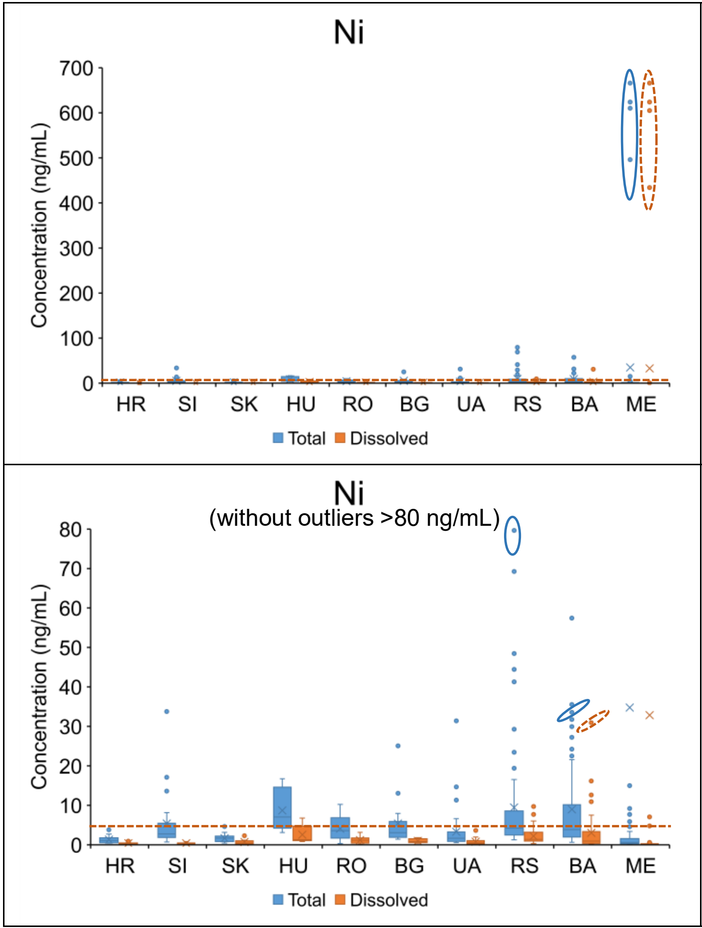
High concentrations of total Cr were occasionally observed in the Ibar River at the Batrage sampling site in Serbia, where elevated Cr and Ni levels arise from natural sources in serpentinite rocks. Cr is almost exclusively bound to particulate matter in river water, with the dissolved Cr content representing only 0.2% of its total concentration. A similar pattern is observed for Cr in the Borska River at the Rogotina site in Serbia, an area with intensive gold and copper mining activities. Total Cr concentrations range from 23 to 56 ng/mL, while the dissolved Cr fraction represents only 1 to 7% of its total content. At both sampling sites, dissolved Cr concentrations did not exceed the EQS value of

4.7 ng/mL Cr(III). It is assumed that Cr in these river samples is present in the trivalent oxidation state, as no sources of hexavalent Cr were identified at these sampling sites. Data from Figure 7 also show slightly elevated total Cr concentrations (10 to 18 ng/mL) in the river water of the Mjedenički Stream, Montenegro. The concentration of dissolved Cr was slightly lower than its total content and exceeded the EQS value by up to a factor of 3.

At other sampling sites across the region, dissolved Cr concentrations were either below or close to the EQS.

6.1.1.4 Nickel

Total and dissolved Ni concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 7.



Mjedenički Stream (ME) — abandoned zinc and lead mine, rich in sulfide minerals.

Sampling site	Ni (ng/mL)
RIV-MEMP-01T	666
RIV-MEMP-01D	666
RIV-MEMP-02T	624
RIV-MEMP-02D	624
RIV-MEMP-03T	496
RIV-MEMP-03D	434
RIV-MEMP-04T	610
RIV-MEMP-04D	605

Batrage, Ibar River (RS) — the elevated Cr and Ni levels are of natural origin from serpentinite rocks.

Sampling site	Ni (ng/mL)
RIV-RSBA-01T	79,6
RIV-RSBA-01D	1,45

Stanić Rijeka, River Spreča (BA) — municipal influence, cement industry, thermal power plant.

Sampling site	Ni (ng/mL)
RIV-BA-SR-01T	33,6
RIV-BA-SR-01D	30,9

Directive 2013/39/EU – Priority Hazardous Substances
EQS for Ni:
Ni……………………………………………………4 ng/mL
Refers to bioavailable Ni content

Figure 7: Total and dissolved Ni concentrations in river water samples from EU and non-EU countries within the DRB.

It should be noted that only dissolved Ni concentrations were determined, and bioavailable Ni was not calculated. A comparison to the $EQS_{bioavailable}$ was made based on dissolved Ni concentrations, which are higher than the bioavailable Ni content.

The data in Figure 7 show that the concentrations of total and dissolved Ni in the water of the Mjedenički Stream, Montenegro, are extremely high (500–670 ng/mL). This area is naturally enriched with sulfide minerals that undergo intensive leaching through complex physicochemical and microbiological processes, leading to the release of Ni from mineral matrices. The dissolved Ni content is nearly identical to the total Ni concentration. The $EQS_{bioavailable}$ (4 ng/mL Ni) is exceeded by more than

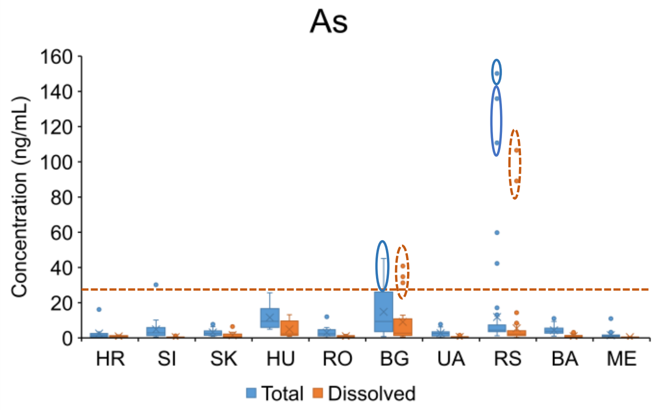
150 times, raising significant environmental concerns, even though the bioavailable Ni fraction was not calculated and is lower than the dissolved Ni content.

Figure 8 also shows that, despite the high total Ni concentration (80 ng/mL) in the Ibar River at the Batrage sampling site in Serbia, the Ni originating from natural serpentinite sources is predominantly associated with particulate matter. Due to the poor solubility of Ni, the dissolved fraction represents only about 2% of the total concentration, which is well below the EQS value for dissolved Ni (4 ng/mL).

In contrast, at the Stanić Rijeka site in Bosnia and Herzegovina, an area influenced by municipal activities, the cement industry, and a thermal power plant, Ni is highly soluble. Here, the total Ni concentration (34 ng/mL) is nearly equal to the dissolved fraction, which exceeds the EQS by a factor of 8.5. At other sampling sites in Bosnia and Herzegovina, Serbia and Montenegro, dissolved Ni concentrations occasionally slightly exceeded the EQS.

6.1.1.5 Arsenic

Total and dissolved As concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 8.



Rgotina, Borska River (RS) — intensive gold and copper mining.

Sampling site	As (ng/mL)
RIV-RSBR-01T	150
RIV-RSBR-01D	4,60

Draževac, Kolubara River (RS) —lignite open-pit mining and a thermal power plant.

Sampling site	As (ng/mL)
RIV-RSKO-01T	111
RIV-RSKO-01D	90,0
RIV-RSKO-02T	136
RIV-RSKO-02D	107

Butan village, Ogosta River (BG) —processing of the lead and zinc ore mobilized geogenic As.

Sampling site	As (ng/mL)
RIV-BGOG-01T	35,5
RIV-BGOG-01D	34,8
RIV-BGOG-03D	31,3
RIV-BGOG-04T	45,1
RIV-BGOG-04D	40,8

EC Environmental Objectives 272/2009 – Specific Pollutants
EQS for As:
As……………………………………………….25 ng/mL

Figure 8: Total and dissolved As concentrations in river water samples from EU and non-EU countries within the DRB.

As can be seen in Figure 8, total As concentrations in the Borska River at the Rogotina site in Serbia, an area affected by intensive gold and copper mining, are occasionally high, reaching up to 150 ng/mL, while the dissolved As fraction accounts for only about 3% of the total As content.

In contrast, a different behaviour is observed for As in the Kolubara River at the Draževac sampling site in Serbia, which is influenced by lignite open-pit mining and a thermal power plant. Total As concentrations reach up to 140 ng/mL, with the dissolved fraction represents approximately 80% of the total As concentration. The EQS for dissolved As is exceeded by a factor of five, raising environmental concern.

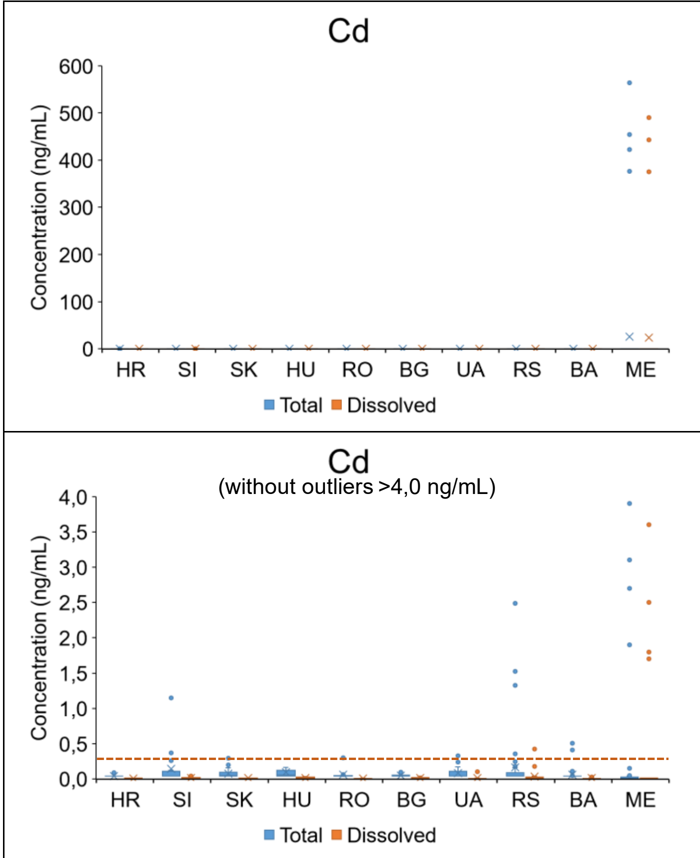
A similar pattern, though at lower As concentrations, is observed in the Ogosta River at the Butan sampling site in Bulgaria, where As is present at concentrations of around 40 ng/mL exclusively in the dissolved form. The EQS is exceeded, at approximately 40 ng/mL.

A similar pattern, though at lower As concentrations, is observed in the Ogosta River at the Butan sampling site in Bulgaria, which is affected by lead and zinc ore processing that has mobilized geogenic As. At this site, As occurs at concentrations of approximately 40 ng/mL, exclusively in the dissolved form, exceeding the EQS by a factor of two.

At other sampling sites across the DRB, dissolved As concentrations were below the EQS.

6.1.1.6 Cadmium

Total and dissolved Cd concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 9.



Mjedenički Stream (ME) — abandoned zinc and lead mine, rich in sulfide minerals.

Sampling site	Cd (ng/mL)
RIV-MEMP-01T	564
RIV-MEMP-01D	490
RIV-MEMP-02T	454
RIV-MEMP-02D	443
RIV-MEMP-03T	422
RIV-MEMP-03D	381
RIV-MEMP-04T	376
RIV-MEMP-04D	375

Mojkovac, Rudnica River (ME) — former lead and zinc ore mining.

Sampling site	Cd (ng/mL)
RIV-MERU-02T	3,1
RIV-MERU-02D	1,8
RIV-MERU-03T	2,7
RIV-MERU-03D	2,5
RIV-MERU-04T	3,9
RIV-MERU-04D	3,6

Rgotina, Borska River (RS) — intensive gold and copper mining.

Sampling site	Cd (ng/mL)
RIV-RSBR-01T	2,49
RIV-RSBR-01D	0,422
RIV-RSBR-03T	1,54
RIV-RSBR-03D	0,179
RIV-RSBR-04T	1,33
RIV-RSBR-04D	0,467

Directive 2013/39/EU – Priority Hazardous Substances

EQS for Cd with regard to water hardness:

<40 mg/L $CaCO_3$ (soft)…………..………≤0.08 ng/mL Cd
40–50 mg/L $CaCO_3$ (soft)…………........0.08 ng/mL Cd
50–100 mg/L $CaCO_3$ (medium-hard.)….0.09 ng/mL Cd
100–200 mg/L $CaCO_3$ (hard)…………...0.15 ng/mL Cd
≥200 mg/L $CaCO_3$ (very hard)………….0.25 ng/mL Cd

Figure 9: Total and dissolved Cd concentrations in river water samples from EU and non-EU countries within the DRB.

As shown in Figure 9, the concentrations of total and dissolved Cd in the Mjedenički Stream in Montenegro are extremely high, reaching 380–500 ng/mL. This stream drains an area naturally enriched in sulfide minerals that undergo intensive leaching through complex physicochemical and microbiological processes, leading to the release of Cd from mineral matrices. Notably, the dissolved Cd concentration is nearly identical to the total concentration, indicating that Cd is almost entirely present in dissolved form. The EQS for dissolved Cd in medium-hard water (0.09 ng/mL) is exceeded by up to 5,500 times, raising serious environmental concerns given the high toxicity of Cd.

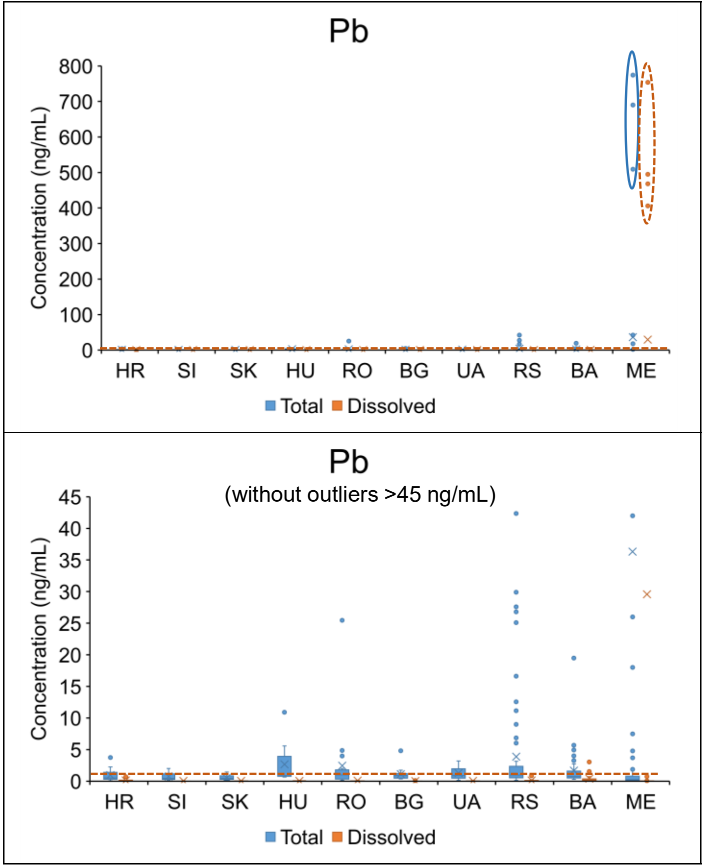
Relatively high Cd concentrations (up to 4 ng/mL) are also observed in the Rudnica River at the Mojkovac site in Montenegro, an area affected by historical lead and zinc ore mining activities. Dissolved Cd accounts for approximately 90% of the total Cd concentration, and the EQS value for dissolved Cd is exceeded by up to 40 times, highlighting a notable environmental concern.

Moderate Cd concentrations were also observed in the Borska River at the Rgotina site in Serbia, where total Cd reaches up to 2.5 ng/mL, while the dissolved fraction is significantly lower, at up to 0.4 ng/mL, exceeding the EQS for about 4 times.

At other sampling sites across the region, dissolved Cd concentrations were below the EQS.

6.1.1.7 Lead

Total and dissolved Pb concentrations in river water samples from both EU and non-EU countries within the DRB are presented in Figure 10.



Mjedenički Stream (ME) — abandoned zinc and lead mine, rich in sulfide minerals.

Sampling site	Pb (ng/mL)
RIV-MEMP-01T	774
RIV-MEMP-01D	754
RIV-MEMP-02T	519
RIV-MEMP-02D	468
RIV-MEMP-03T	690
RIV-MEMP-03D	495
RIV-MEMP-04T	509
RIV-MEMP-04D	406

Directive 2013/39/EU – Priority Hazardous Substances
EQS for Pb:
Pb……………………………………………….1.2 ng/mL
Refers to bioavailable Pb content

Figure 10: Total and dissolved Pb concentrations in river water samples from EU and non-EU countries within the DRB.

It should be noted that only dissolved Pb concentrations were determined, and the bioavailable Pb fraction was not calculated. A comparison to the $EQS_{bioavailable}$ was made based on dissolved Pb concentrations, which are higher than the bioavailable Pb content.

As shown in Figure 10, extremely high concentrations of Pb (up to 770 ng/mL) were determined in the Mjedenički Stream, Montenegro. This is attributed to the intensive leaching of Pb from the mineral phases through complex physicochemical and microbiological processes. The concentration of dissolved Pb accounted for approximately 90% of its total content, exceeding the $EQS_{bioavailable}$ value (1.2 ng/mL Pb) by up to a factor of 440. This raises serious environmental concerns, as Pb is known to be highly toxic. However, since the bioavailable Pb fraction was not calculated, it is likely lower than the dissolved Pb concentration.

Dissolved Pb concentrations at the other sampling sites across the investigated river catchments were in general below the $EQS_{bioavailable}$ value of 1.2 ng/mL and were occasionally slightly exceeded at sampling sites in Bosnia and Herzegovina. It should be noted that only dissolved Pb concentrations were determined and that bioavailable Pb was not calculated. A comparison to the EQS was made based on dissolved Pb concentrations, which are higher than the bioavailable Pb content.

Data from a one-year monitoring campaign conducted in six EU and four non-EU countries showed that total and dissolved concentrations of Zn, Cu, Ni, Cr, As, Cd, and Pb in river water were generally comparable to previously reported values from the Sava and Evrotas rivers (Milačič et al., 2017, 2019). Dissolved metal concentrations were also comparable to those reported for rivers in the Danube catchment (Liška et al., 2015), the Sava River in Slovenia and Croatia (Lučić et al., 2022), and the Chao Phraya River (Niampradit et al., 2024), except at known hotspots (Table 6).

Table 6: Concentrations of elements in river waters under basic-flow conditions compared with the literature data.

River/ Location	River water	Pb (ng/mL)	Cd (ng/mL)	As (ng/mL)	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	Reference
Chao Phraya / Thailand	Dissolved	<LOQ–8.6	<LOQ	/	<LOQ–16	<LOQ–3.2	<LOQ–5.6	2.4–20	Niampradit et al., 2024
Danube catchment	Dissolved	0.20–8.1	<0.01–1.1	1.1–5.3	0.29–67	0.78–230	1.1–283	1.0–61	Liška et al., 2015
Zagyva, Koppány/ Hungary	Dissolved	<0.015–1.2	<0.004–0.038	1.05–103	0.076–4.4	0.903–3.2	0.998–7.0	<0.070–14	Milačič et al., 2023
Sava/Slovenia, Croatia	Dissolved	0.035–0.235	0.008–0.067	0.294–0.830	0.143–2.1	0.269–1.6	0.314–3.7	0.843–12	Lučić et al., 2022
Sava / Sava catchment	Total	<0.15–2.0	<0.04–0.05	0.20–3	0.50–12	1–35	0.40–6.0	0.40–8.0	Milačič et al., 2017
	Dissolved	<0.015–0.30	<0.004–0.015	0.02–1.5	0.10–0.50	0.1–5.5	0.2–2.0	0.2-5.0	
Evrotas / Greece	Total	<0.15–0.25	<0.04–0.070	<0.10–0.18	0.02–0.8	0.20–24	0.20–0.50	0.80–6.0	Milačič et al., 2019
	Dissolved	<0.015–0.050	<0.004–0.070	<0.01–0.015	0.2–0.7	0.10–6.0	0.015–0.20	<0.07–0.15	

Extremely high metal concentrations, similar to those observed in the Medjenički Stream in Montenegro, have also been reported for the Tinto River in Spain as a result of historical sulfide ore mining. Due to its very low pH (approximately 2.5) and the presence of *Acidithiobacillus* bacteria, which promote natural bioleaching from waste ore deposits formed over centuries of mining, the Tinto River is highly contaminated with metals (Olías et al., 2020).

Average, median, minimum, and maximum concentrations of elements in river waters under base-flow conditions from the Danube Hazard m^3c and Tethys projects are summarized in Table 7.

Table 7: Average, median, minimum, and maximum concentrations of elements in river waters under base-flow conditions from the Danube Hazard m^3c and Tethys projects.

Total metal concentrations in river water							
Danube Hazard m^3c	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	As (ng/mL)	Cd (ng/mL)	Pb (ng/mL)
Average	2,91	8,21	16,8	117	2,86	0,380	1,88
Median	1,65	4,19	2,79	10,4	2,33	0,040	0,966
Minimum	0,164	0,168	0,460	0,233	0,178	0,040	0,119
Maximum	23,0	105	599	3942	26,4	6,80	14,7

Dissolved metal concentrations in river water							
Danube Hazard m^3c	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	As (ng/mL)	Cd (ng/mL)	Pb (ng/mL)
Average	0,362	1,35	3,39	89,9	1,74	0,258	0,083
Median	0,120	1,25	1,19	3,90	0,893	0,007	0,043
Minimum	0,006	0,006	0,196	0,060	0,129	0,004	0,015
Maximum	4,44	4,72	44,4	3374	10,3	5,95	1,15

Total metal concentrations in river water							
Tethys	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	As (ng/mL)	Cd (ng/mL)	Pb (ng/mL)
Average	5,33	12,10	22,46	4784	5,65	5,25	9,07
Median	2,37	2,43	2,76	6,94	3,03	0,040	0,696
Minimum	0,062	0,090	0,100	0,493	0,090	0,010	0,060
Maximum	163	666	2260	506690	150	564	774

Dissolved metal concentrations in river water							
Tethys	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	As (ng/mL)	Cd (ng/mL)	Pb (ng/mL)
Average	0,55	7,98	5,32	4472	2,27	4,82	6,17
Median	0,219	0,687	0,883	1,52	0,736	0,010	0,060
Minimum	0,014	0,027	0,016	0,070	0,064	0,004	0,007
Maximum	14,0	666	496	499520	107	490	754

A comparison of results from the Danube Hazard m^3c and Tethys projects shows that the maximum concentrations of elements, both total and in the soluble fraction, are significantly higher at the sampling sites analyzed within the Tethys project. In Tethys, these elevated values are associated with several contamination hotspots, most notably the Mjedenički Stream and the Rudnica River in Montenegro, as well as the Borska River in Serbia. As a result, average concentrations are also considerably higher at Tethys sampling sites. It is evident that very high concentrations of Zn and Cu were also measured within the Danube Hazard m3c project. These concentrations are associated with the sampling site on the Cisla River, a tributary of the Vișeu River in Romania. Zn concentrations ranged from 1,400 to 4,000 ng/mL, while Cu concentrations ranged from 60 to 270 ng/L. These elevated Zn and Cu levels are linked to an area with a very high natural background and historical mining activities in the area. In contrast, median concentrations, which minimize the influence of outliers (extreme values), are quite similar between the Danube Hazard m3c and Tethys datasets. This suggests that hotspots at sampling sites in the Tethys project contribute substantially to poorer river water quality, particularly in Montenegro and Serbia, and to a lesser extent in Bosnia and Herzegovina, while in the Danube Hazard m^{3}c project the main hotspot is located in Romania.

6.1.2 Metal concentrations in wastewater samples

Total metal concentrations in wastewater samples from both EU and non-EU countries within the DRB are presented in Figure 11.

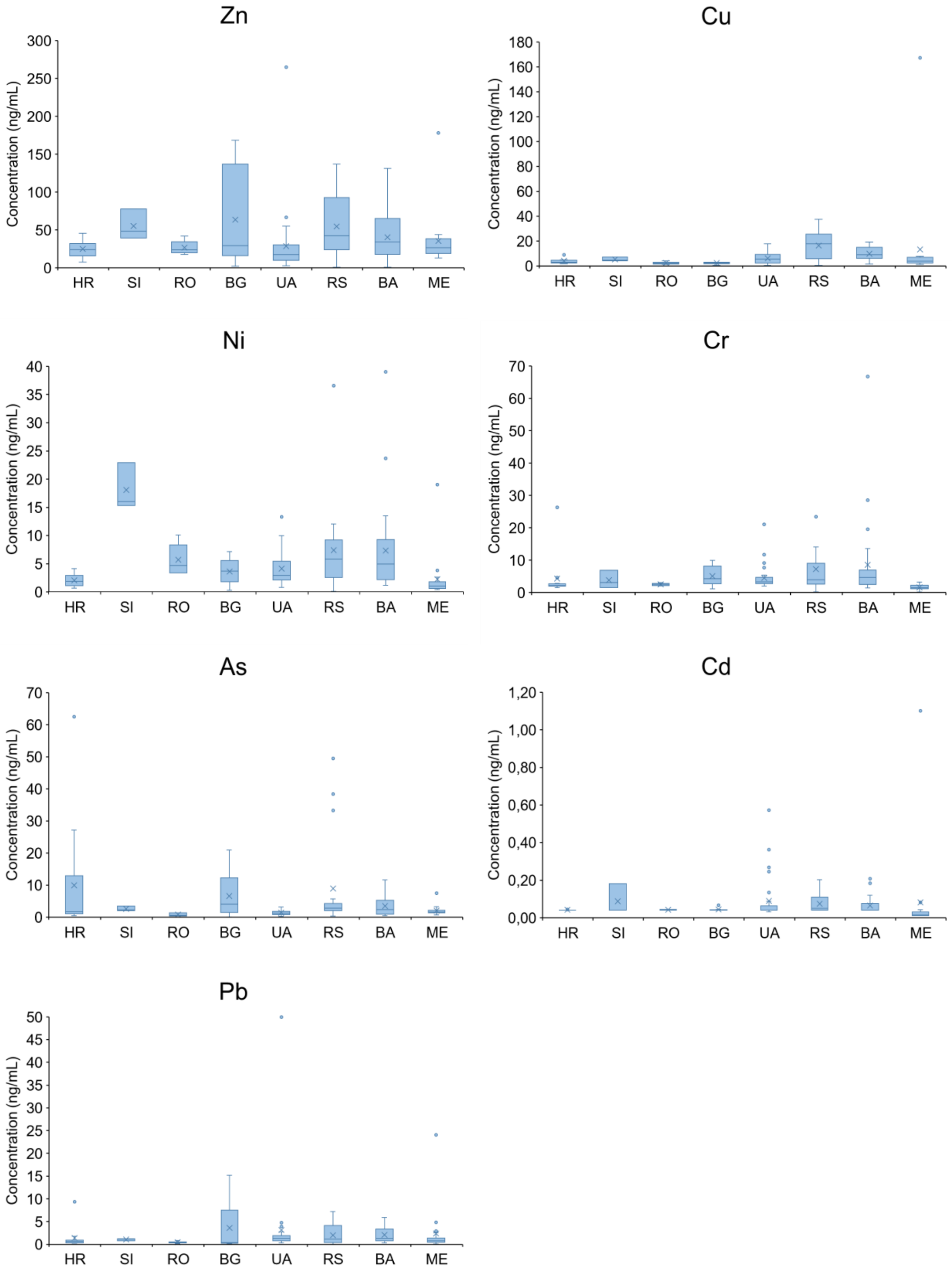


Figure 11: Total metal concentrations in wastewater samples from EU and non-EU countries within the DRB.

The new Urban Waste Water Treatment Directive (EU) 2024/3019 does not establish limit values for metals such as Cd, Pb, Cu, Zn, Cr, Ni, or As in treated wastewater. Rather than defining specific concentration thresholds, the directive concentrates on ensuring that urban wastewater is properly collected, treated, and discharged in ways that safeguard both environmental quality and public health. Its primary aim is to guarantee treatment performance that prevents negative impacts on receiving water bodies and supports the broader goals of EU water policy.

To meet these objectives, European countries rely on their national regulatory frameworks, which set requirements for the quality of treated wastewater released into surface waters. A comparison of Tethys project monitoring data with Slovenian national legislation (Regulation on the Emission of Substances and Heat, Official Gazette No. 157/22, 2022) indicates that all evaluated wastewater treatment plants complied with the metal EQS limits, which are: 500 ng/mL for Cr, 50 ng/mL for Ni, 500 ng/mL for Cu, 2000 ng/mL for Zn, 100 ng/mL for As, 25 ng/mL for Cd, and 500 ng/mL for Pb.

Average, median, minimum, and maximum concentrations of elements in wastewaters from the Danube Hazard m^{3}c and Tethys projects are summarized in Table 8 .

Table 8: Average, median, minimum, and maximum concentrations of wastewaters from the Danube Hazard m^{3}c and Tethys projects.

Total metal concentrations in wastewater							
Danube Hazard m^{3}c	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	As (ng/mL)	Cd (ng/mL)	Pb (ng/mL)
Average	43,3	40,9	317	2195	9,71	6,28	11,7
Median	4,22	9,67	25,3	105	2,18	0,127	3,37
Minimum	0,220	0,060	0,801	8,750	0,201	0,036	0,148
Maximum	2307	1501	7879	51599	461	197	208

Total metal concentrations in river water							
Tethys	Cr (ng/mL)	Ni (ng/mL)	Cu (ng/mL)	Zn (ng/mL)	As (ng/mL)	Cd (ng/mL)	Pb (ng/mL)
Average	5,25	5,18	8,50	38,69	4,18	0,07	2,28
Median	2,93	3,10	5,10	26,30	1,64	0,04	0,87
Minimum	0,14	0,10	0,13	0,70	0,10	0,01	0,06
Maximum	66,7	39,0	167	265	62,4	1,10	50,0

A comparison of concentrations measured in the Danube Hazard m3c and Tethys projects shows that the maximum concentrations of elements, and consequently the average concentrations, are significantly higher in the Danube Hazard m3c project. This is related to mining activities in the Cisla River area in Romania, where drainage waters from mining operations are discharged directly into the river without treatment.

Median concentrations, which minimize the influence of outliers, are still slightly higher in the Danube Hazard m3c project compared to the Tethys dataset.

6.1.3 Metal concentrations in groundwater samples

Dissolved metal concentrations in groundwater samples from both EU and non-EU countries within the DRB are presented in Figure 12.

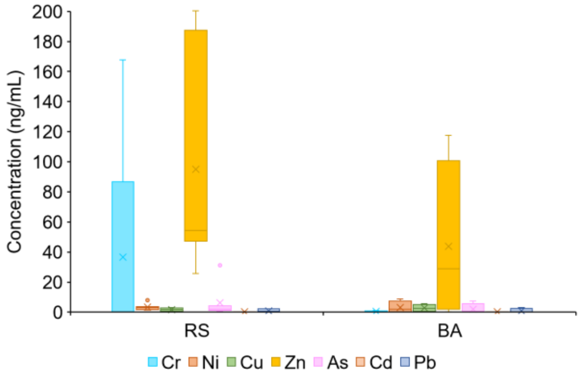


Figure 12: Dissolved metal concentrations in groundwater samples from Serbia and Bosnia and Herzegovina.

The proposed EU Groundwater Directive (2024) offers guidance for Member States on setting threshold values for pollutants in groundwater. Nevertheless, it does not define specific threshold values for metals such as Cd, Pb, Cr, Ni, Zn, Cu, and As. Elevated Cr and Zn concentrations (up to 80 and 180 ng/mL, respectively) were determined in groundwater samples in Serbia. The elevated contaminant levels can be attributed to direct inputs from the Galovica Canal (Figure 13), emissions from nearby highways, wastewater from the Surčin and Ledine settlements, and agricultural practices. In Bosnia and Herzegovina, Zn concentrations reached up to 100 ng/mL, likely influenced by the Bijeljina waste landfill. These groundwater sources are contaminated and not suitable for human consumption.

Figure 13: Galovica Canal in Serbia, influenced by nearby highway emissions, wastewater from the settlements of Surčin and Ledine, and surrounding agricultural activities.

6.1.4 Metal concentrations in urban stormwater runoff samples

Total metal concentrations in urban stormwater runoff samples from Hungary are presented in Figure 14.

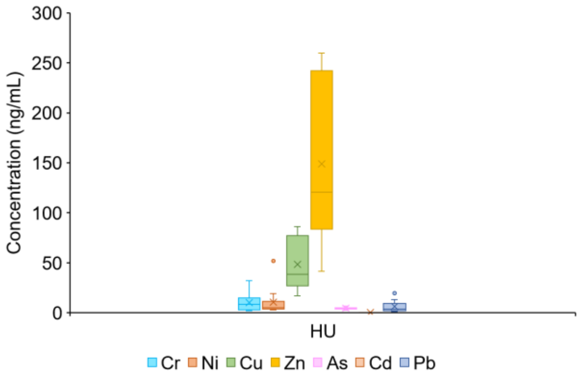


Figure 14: Total metal concentrations in urban stormwater runoff samples from Hungary.

As shown in Figure 14, urban stormwater runoff samples collected in Hungary exhibited Zn concentrations of up to 250 ng/mL, primarily due to ZnO additives in car tires. Cu concentrations reached up to 80 ng/mL, linked to Cu released from automotive brake components. Additionally, Cr and Ni concentrations of up to 60 ng/mL and 20 ng/mL, respectively, are associated with brake wear and industrial emissions. These runoff waters are discharged into rivers and can contribute to overall water pollution.

6.2 Results of PFAS and pharmaceutical analyses

6.2.1 Overview of detection frequency across compartments and countries

Figure 15 provides a compact overview of the detection frequency for the PFAS compounds, namely the proportion of samples with measured values above LOQ, in the investigated compartments and in the different countries. A significant portion of the targeted PFAS, particularly long-chain compounds, were not detected in most samples. Detection rates were generally uniform across countries, with the notable exception of Montenegro (ME), which exhibited a lower overall detection rate, probably attributable to its different analytical methodology. For the PFCA group, detection rates decreased with increasing chain length. In the PFSA group, only PFBS, PFHxS, and PFOS were frequently detected, while others were rarely or never detected. The other PFAS substances showed consistently low to zero detection rates. Only two substances (6:2 FTS and FBSA) were frequently detected, with higher occurrences in upstream Danube countries (SK, HU, SI, HR, RS) compared to downstream countries (UA, RO, BG, BA).

Comparing water compartments, groundwater samples had the lowest overall detection rates, whereas stormwater samples showed the highest detection rates, including for compounds that were infrequently detected in other compartments.

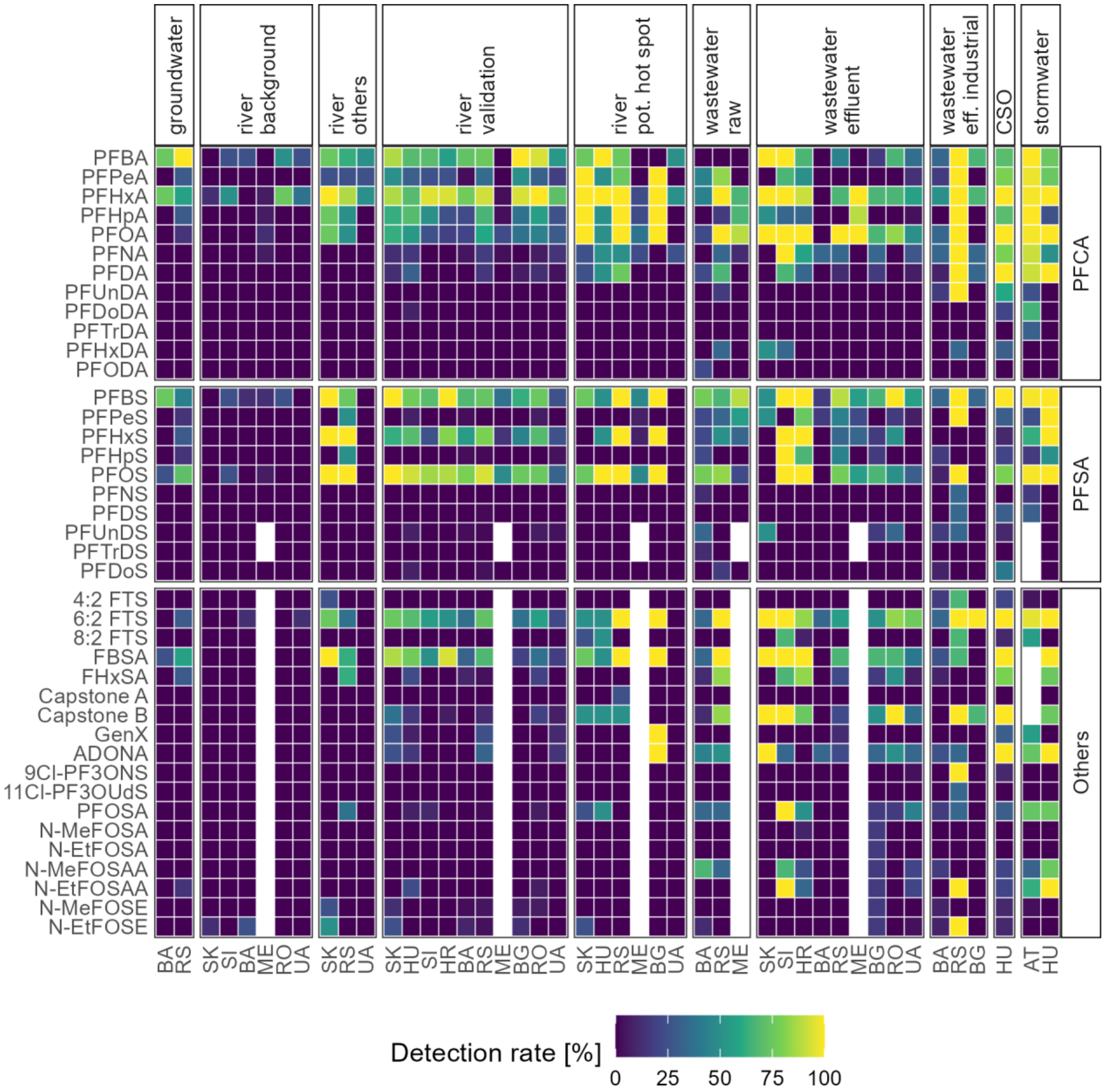


Figure 15: Detection frequency of PFAS compounds across compartments and countries. Detection is defined here as measurement above LOQ.

Figure 16 provides a compact overview of the detection frequency for pharmaceuticals. Pharmaceuticals displayed a distinct pattern of detection than PFAS. In surface waters, bezafibrate, citalopram, and Ibuprofen had low detection rates, while others were frequently detected. Montenegro (ME) and Slovakia (SK) generally showed lower detection rates than other countries. In wastewater, nearly all substances had very high detection rates, except for bezafibrate except in Slovenia (SI). Another notable exception included Ibuprofen in SK samples and all parameters in BA samples. CSO and stormwater samples exhibited very high detection rates across most compounds. In contrast, groundwater samples had very low detection rates, apart from metoprolol and trimethoprim, which were consistently detected in samples from RS and BA.

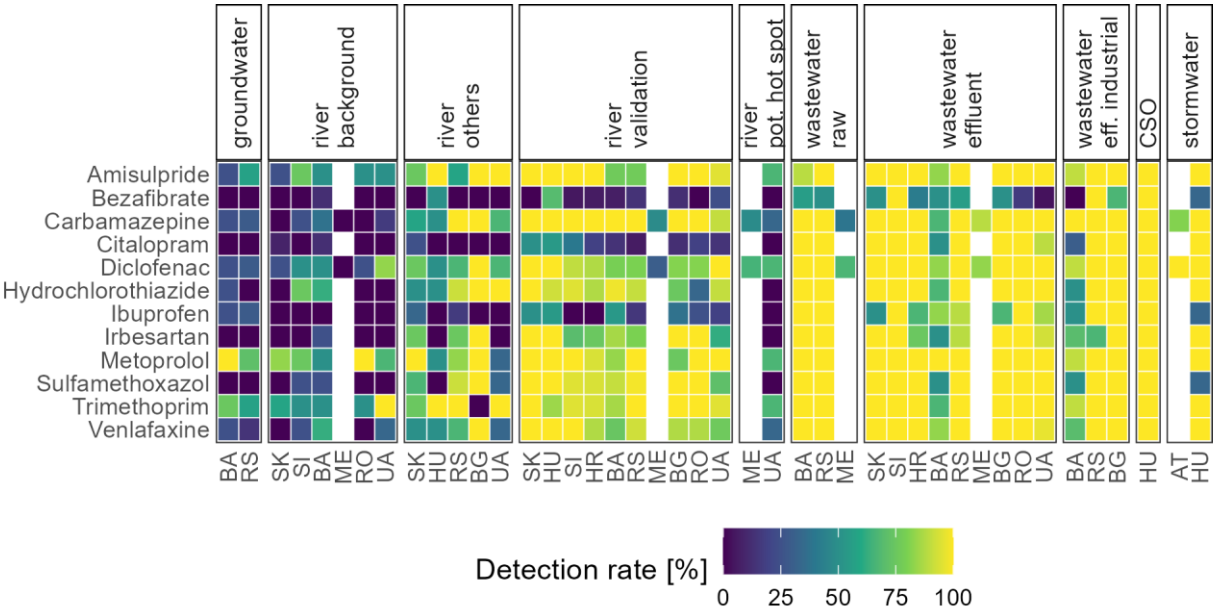


Figure 16: Detection frequency of pharmaceuticals across compartments and countries. Detection is defined here as measurement above LOQ.

6.2.2 PFAS and pharmaceutical concentrations in river water samples across countries

6.2.2.1 PFAS in river water samples across countries

The ranges of measured concentrations for the most detected PFAS compounds at different types of river sampling sites across countries are presented in Figure 17, Figure 18, Figure 19 and Figure 20.

Within the PFCA group, the potential river hotspot sites exhibited the highest concentrations, thus confirming their status as hotspots. In the case of PFNA and PFDA, these compounds were only detected at the hotspot sites. River background sites exhibited the lowest concentrations across all compartments. In the PFSA group, the hotspots in Serbia for PFHxS and PFOS showed median concentrations similar to those at validation sites. However, the concentrations at other sampling sites were significantly higher, indicating different types of contamination sources and thus PFAS profiles at these hotspots.

PFBA concentrations were highest in Hungary (HU) and lowest in Ukraine (UA). PFPeA was highest in Slovakia (SK), Bulgaria (BG), and Romania (RO), and lowest in Ukraine. For PFHpA and PFOA, Hungary, Slovakia, and Serbia (RS) showed the highest mean concentrations, while other countries showed medians below the limit of detection (LOD). PFOA levels were highest in HU and RS and lowest in Croatia (HR). UA showed a generally low mean, but several outliers reached concentrations comparable to those in Hungary.

For the PFSA group, PFBS concentrations were highest in Hungary, Slovakia, and Bulgaria, and lowest in Ukraine. PFHxS showed the highest mean concentrations in Romania and Serbia, while Bulgaria and Ukraine were lowest. PFOS was highest in Hungary, Romania, and Serbia, and lowest in Ukraine.

Other PFAS substances exhibited a wide range of concentrations or were predominantly below the limit of quantification (LOQ). 6:2 FTS and PFBSA showed a broad range of measured values, with only Hungary, Slovakia, and Serbia having median concentrations above the LOQ. For the remaining substances, a few outliers belonged to different countries with no discernible common pattern and were primarily from sites classified as validation or hotspot sites.

The observed differences in data distributions for certain compounds (e.g., Capstone B in Slovakia; GenX and ADONA in Serbia) are due to the application of the Regression on Order Statistics (ROS) method for datasets meeting the necessary criteria; otherwise, values below LOQ were represented as half the LOQ. For N-EtFOSE, all countries showed values predominantly below the LOQ, except for Slovakia, which showed the highest values, all above the LOQ.

A trend was observed in the PFCA group where shorter-chain compounds had more measurements above the LOQ. PFBA levels in Hungary, Bulgaria, and Romania were higher than in other countries. For other parameters, differences between countries were less pronounced.

It is notable that the measured values in Montenegro (ME) were systematically much lower than the ones in the other countries. This might be due to significant differences in the analytical methods applied, leading to reduced comparability. Therefore, these samples are excluded from compartment-wise comparisons in further analyses in order to avoid artificial underestimations.

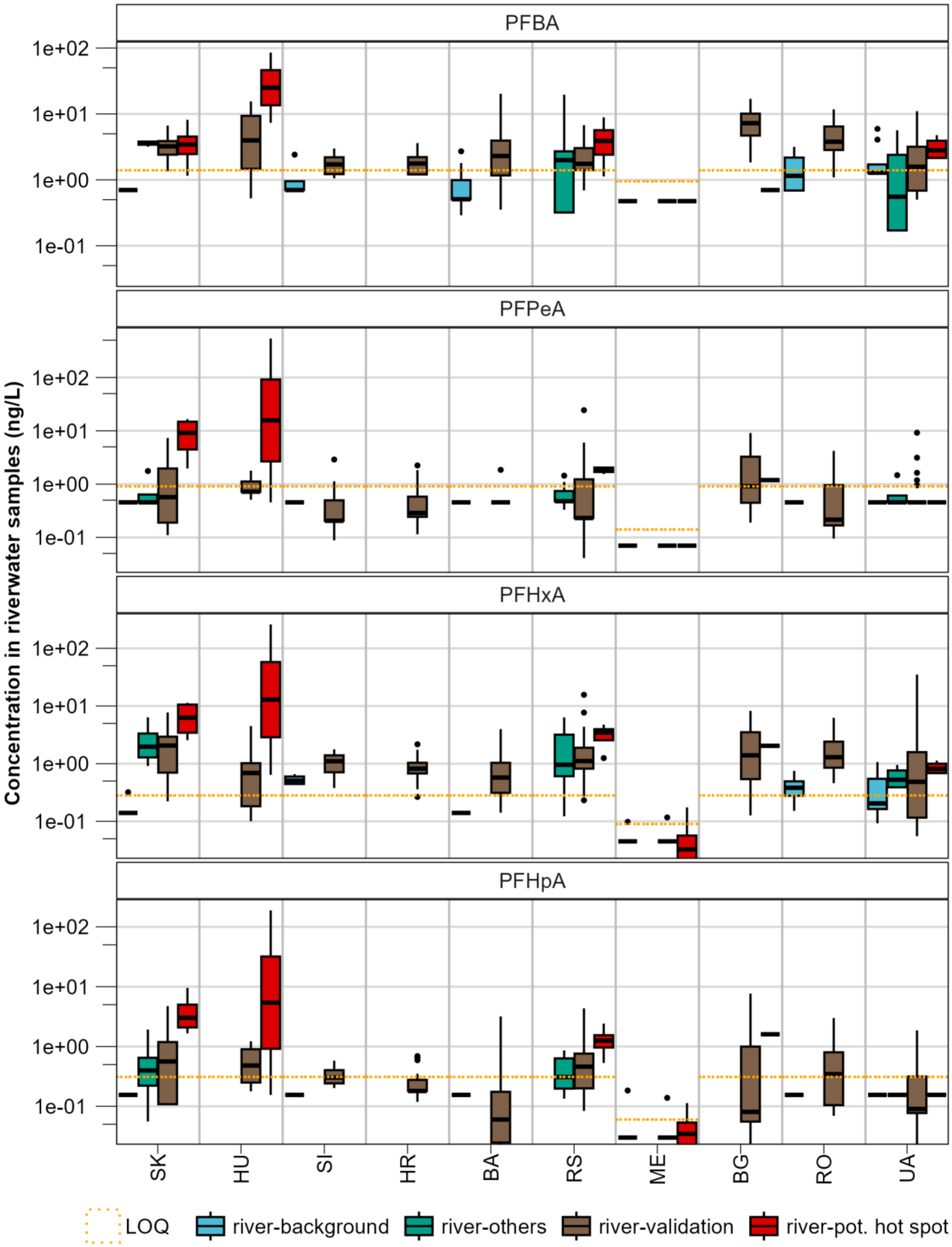


Figure 17: Distribution of PFAS concentrations measured in different types of river sampling sites. "river-pot. hot spot": locations initially identified as potential hotspots.

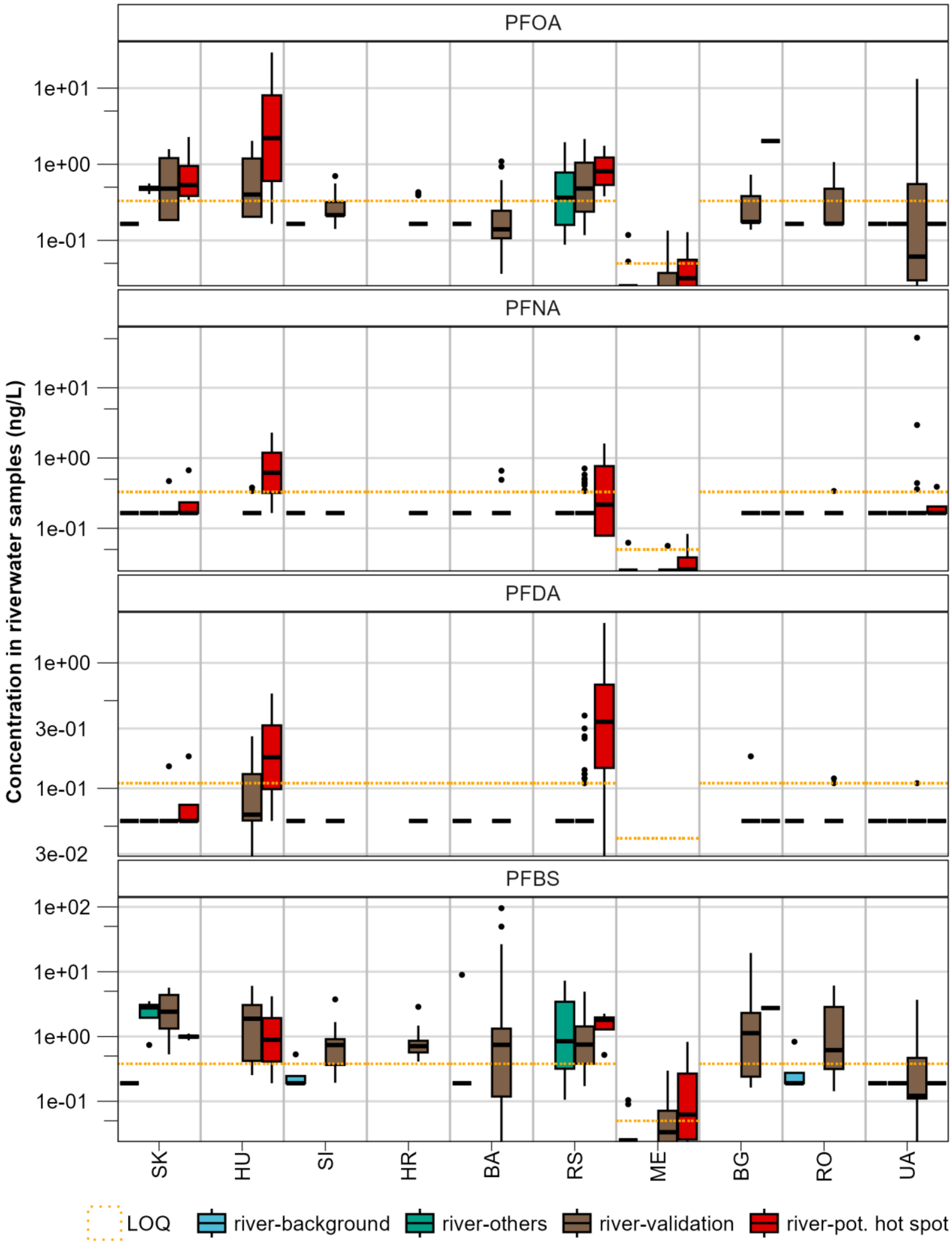


Figure 18: Distribution of PFAS concentrations measured in different types of river sampling sites. "river-pot. hot spot": locations initially identified as potential hotspots.

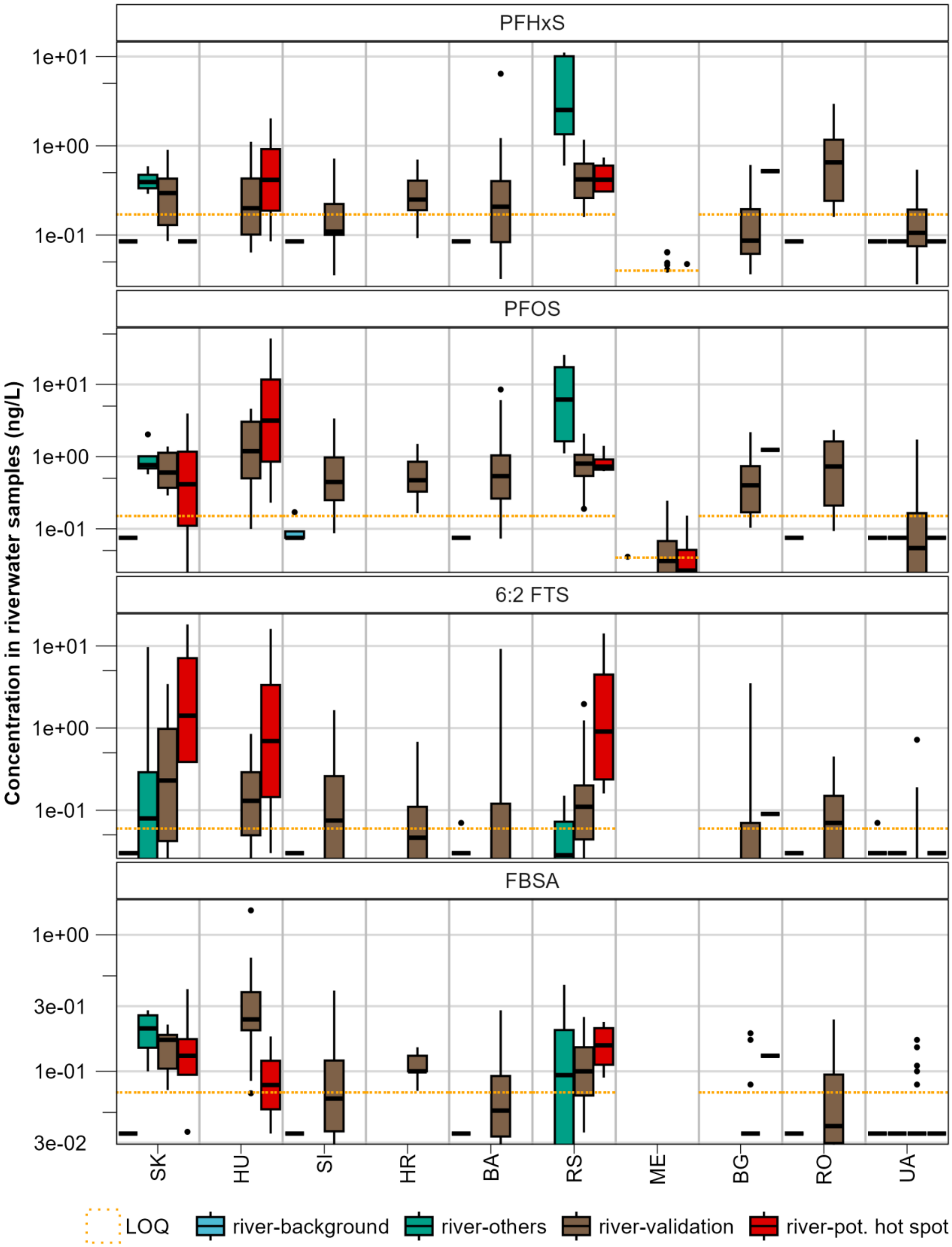


Figure 19: Distribution of PFAS concentrations measured in different types of river sampling sites. "river-pot. hot spot": locations initially identified as potential hotspots.

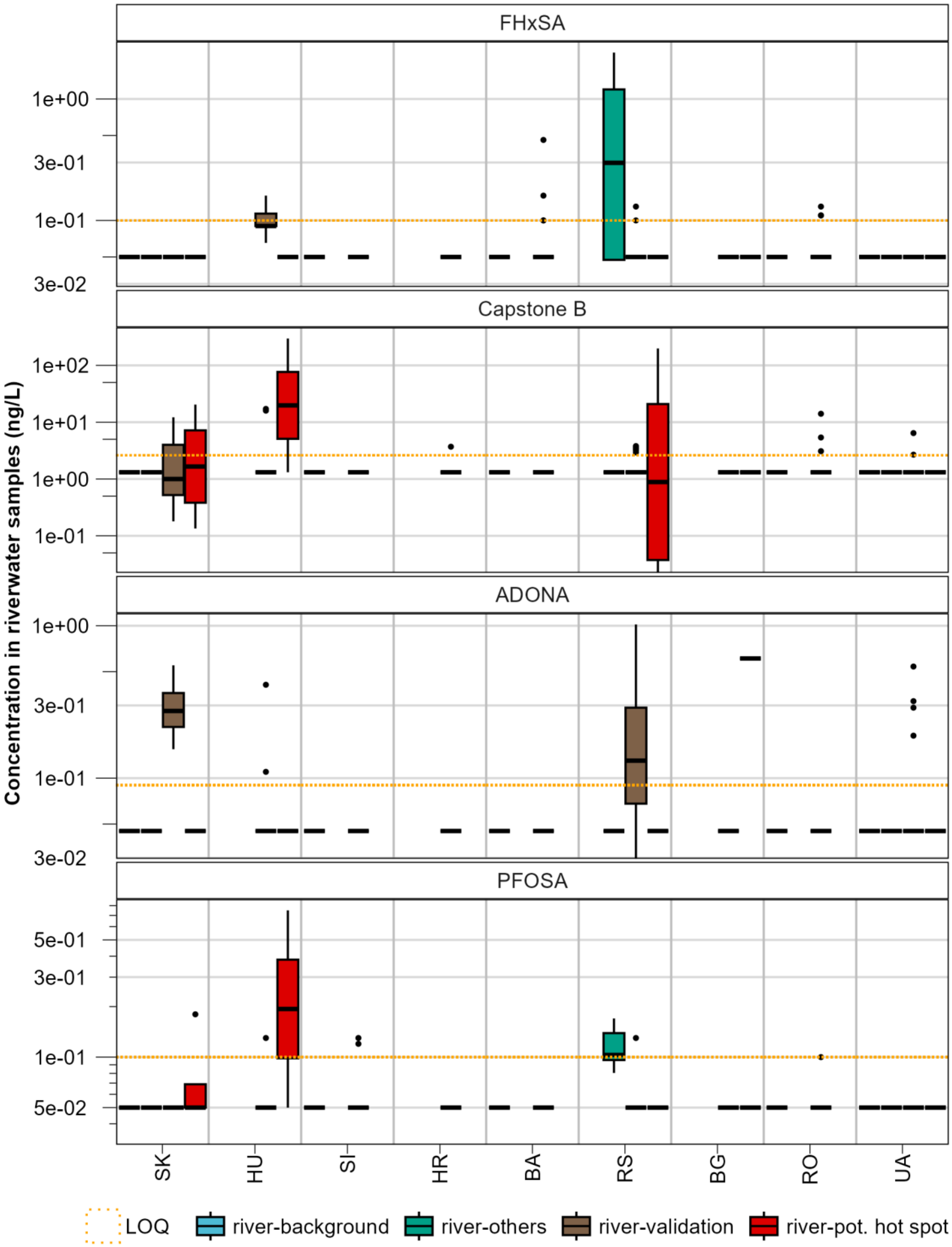


Figure 20: Distribution of PFAS concentrations measured in different types of river sampling sites. "river-pot. hot spot": locations initially identified as potential hotspots.

6.2.2.2 Pharmaceuticals in river water samples across countries

Figure 21 shows that pharmaceutical concentrations in river samples varied widely, from 1 ng/L to 10,000 ng/L. Although background sites generally had lower concentrations, individual measurements at these locations occasionally exceeded the mean concentrations at validation and hotspot sites. Potential hotspot sites had significantly lower concentrations than other sites, indicating that the classification of hotspot was not correct for the pharmaceuticals investigated in this monitoring programme. Therefore, in further analyses, the category "hotspot" for pharmaceuticals was removed and merged with the "others" category, which includes the hotspot river sites identified as such due to high contamination of metals or PFAS.

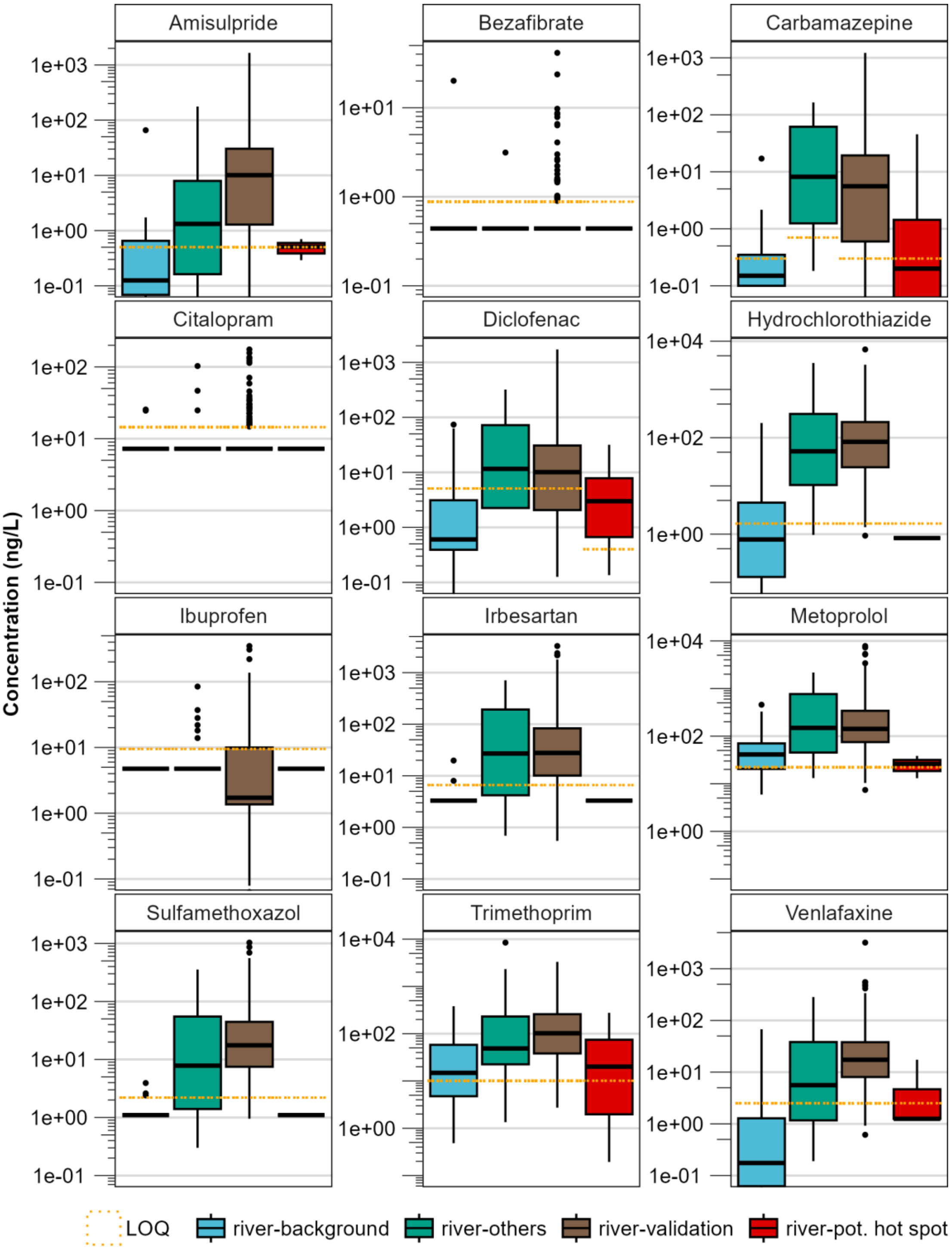


Figure 21: Distribution of pharmaceuticals concentrations measured in different types of river sampling sites. "river-pot. hot spot": locations initially identified as potential hotspots.

Pharmaceutical concentrations were generally lower in UA, RO, ME, BA, RS, SI, and HR, and higher in HU, SK, RO, BG, SI, and HR, though this varied by substance (Figure 22, Figure 23, Figure 24). The systematically much lower concentrations in ME (over an order of magnitude) are likely an artefact of the different analytical method. For some pharmaceuticals (e.g. hydrochlorothiazide, trimethoprim), differences between countries were minor. For others (e.g. amisulpride, irbesartan), differences were substantial. For a subset of compounds (ibuprofen, bezafibrate, citalopram), the high number of measurements below LOQ does now allow carrying out meaningful comparisons between countries.

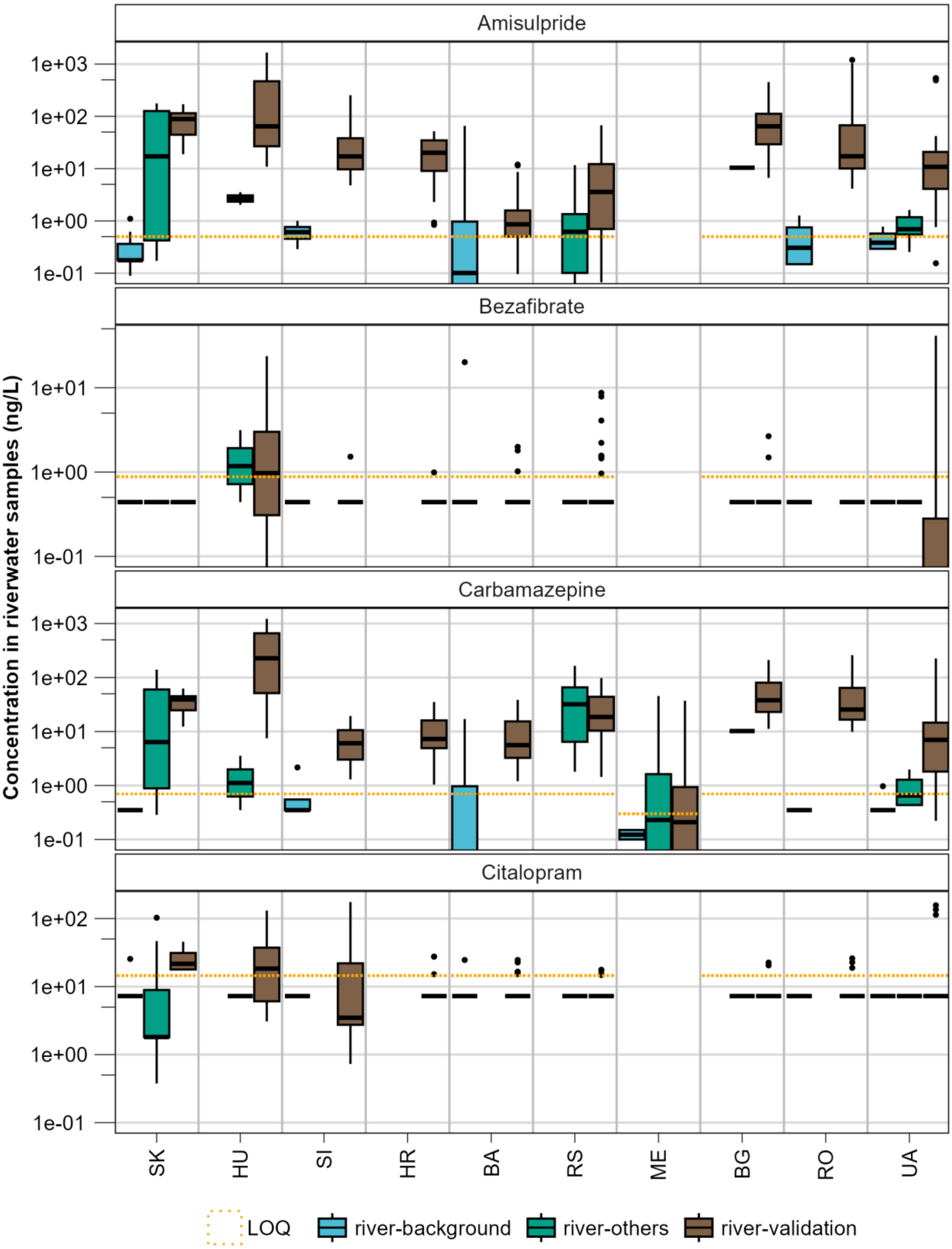


Figure 22: Distribution of pharmaceuticals concentrations measured in river samples of different countries.

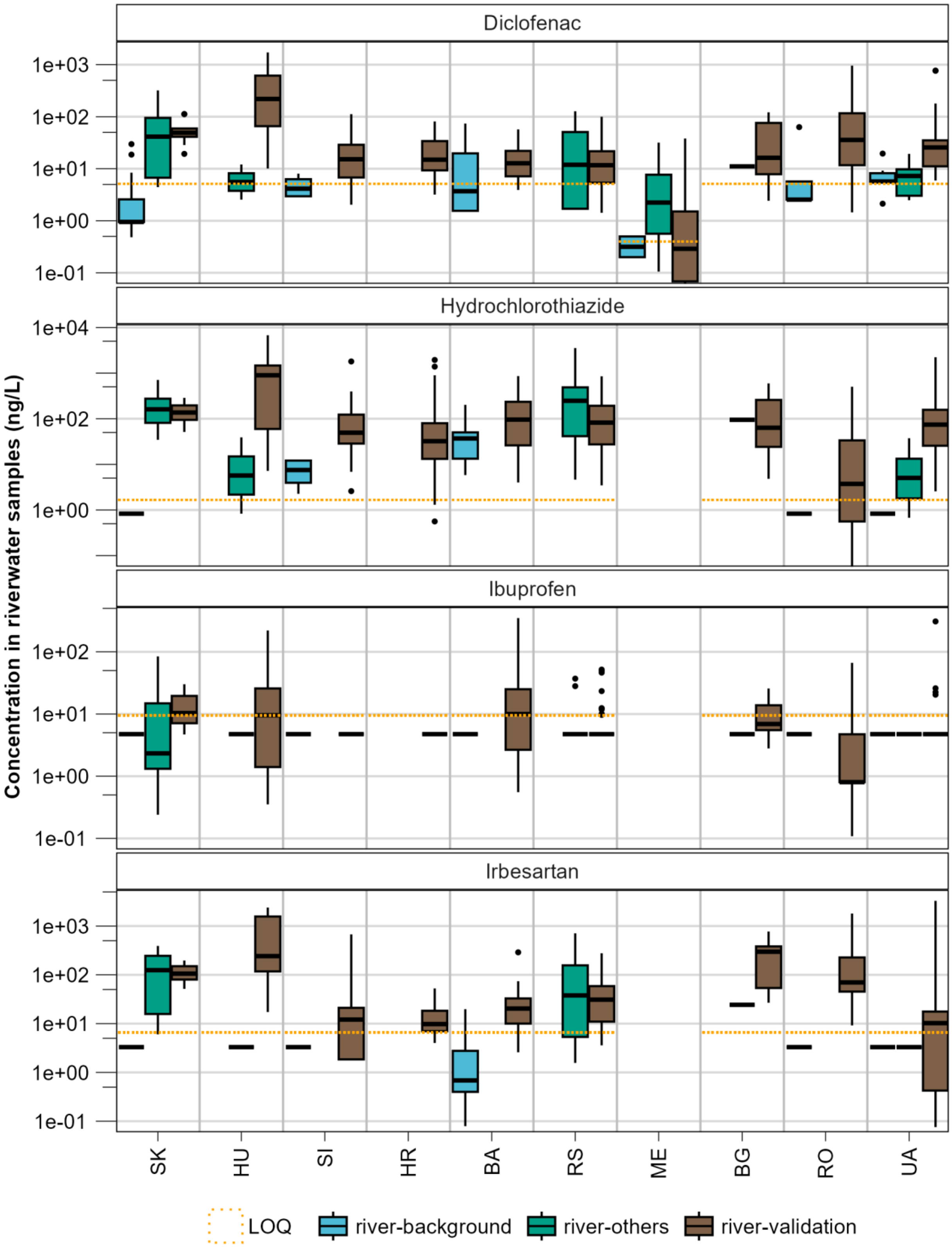


Figure 23: Distribution of pharmaceuticals concentrations measured in river samples of different countries.

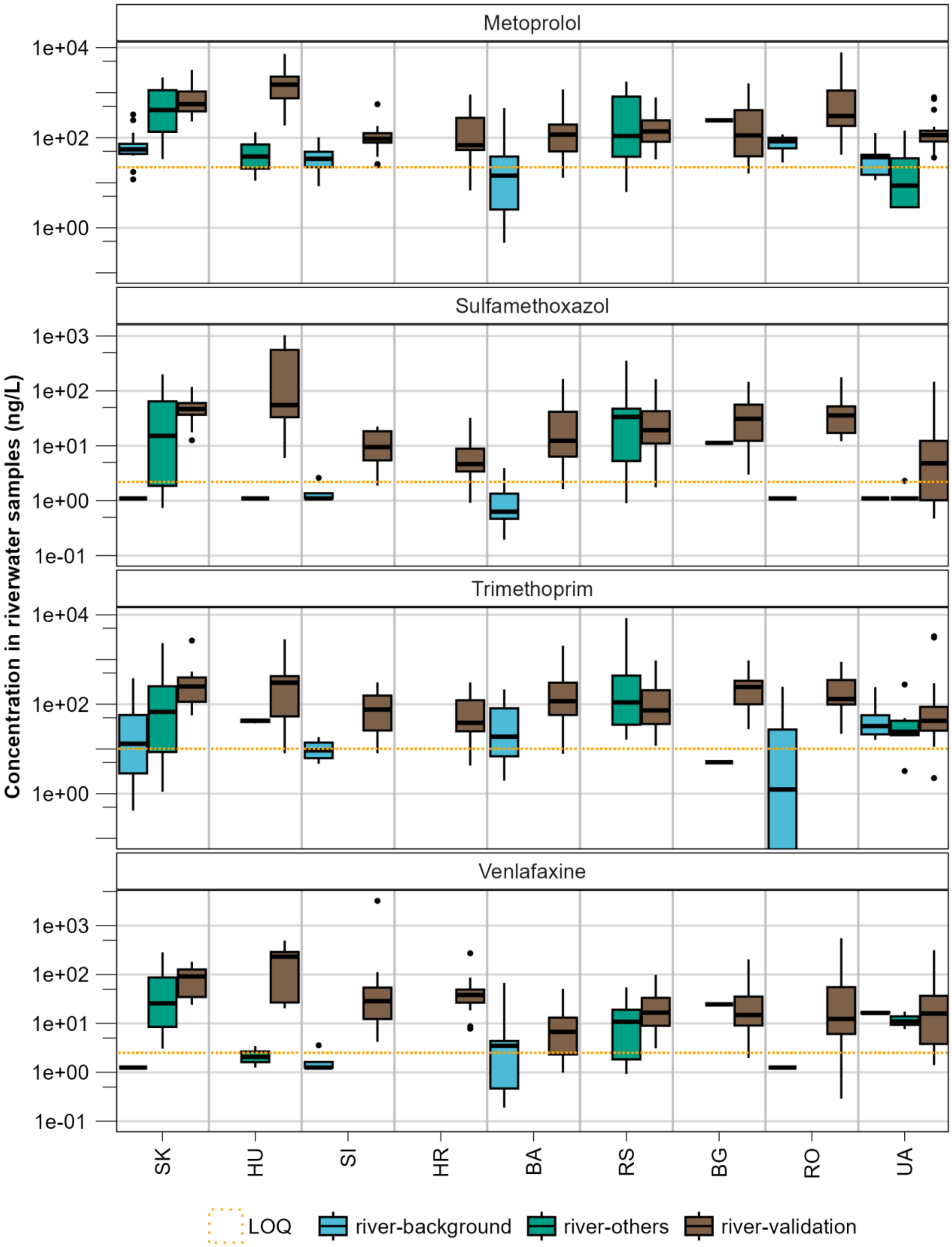


Figure 24: Distribution of pharmaceuticals concentrations measured in river samples of different countries.

6.2.3 PFAS and pharmaceutical concentrations in wastewater samples across countries

6.2.3.1 PFAS in wastewater samples across countries

The detectability of PFAS in wastewater varied by country, with most substances found below the LOQ and occasional measurements above it (Figure 25, Figure 26, Figure 27 and Figure 28). ADONA concentrations were significantly higher only in SK. PFOSA, N-MEFOSAA, and N-EtFOSAA were highest in SI and RS, though outliers from other countries reached similar maximum values. SI and HR exhibited the highest concentrations for several compounds, including PFBS, PFHpS, PFOS, 6:2 FTS, FHxSA, and Capstone B. HR had the highest PFHxS, while SK had the highest PFUnDS. Some outliers spanned more than two orders of magnitude above the LOQ (e.g., 4:2 FTS, detected only in BA and RS.

For the PFCA group, results varied strongly between countries. PFPeA was exceptionally high in all RS raw and industrial effluent wastewater samples and in one effluent sample from UA, while in other countries it was an order of magnitude lower and mostly below the LOQ. For PFHxA, SI had the highest median concentration, though a few industrial effluent wastewater samples from RS were outliers nearly two orders of magnitude higher. Similarly, SI showed higher concentrations for PFNA. SK and SI showed higher concentrations for PFBA. Generally, differences between countries diminished with increasing PFCA chain length as concentrations approached the LOQ.

It is notable that the measured values in Montenegro (ME) were systematically much lower than the ones in the other countries. This might be due to significant differences in the analytical methods applied or issues with the matrix, leading to reduced comparability. Therefore, these samples are excluded from compartment-wise comparisons in further analyses in order to avoid underestimations.

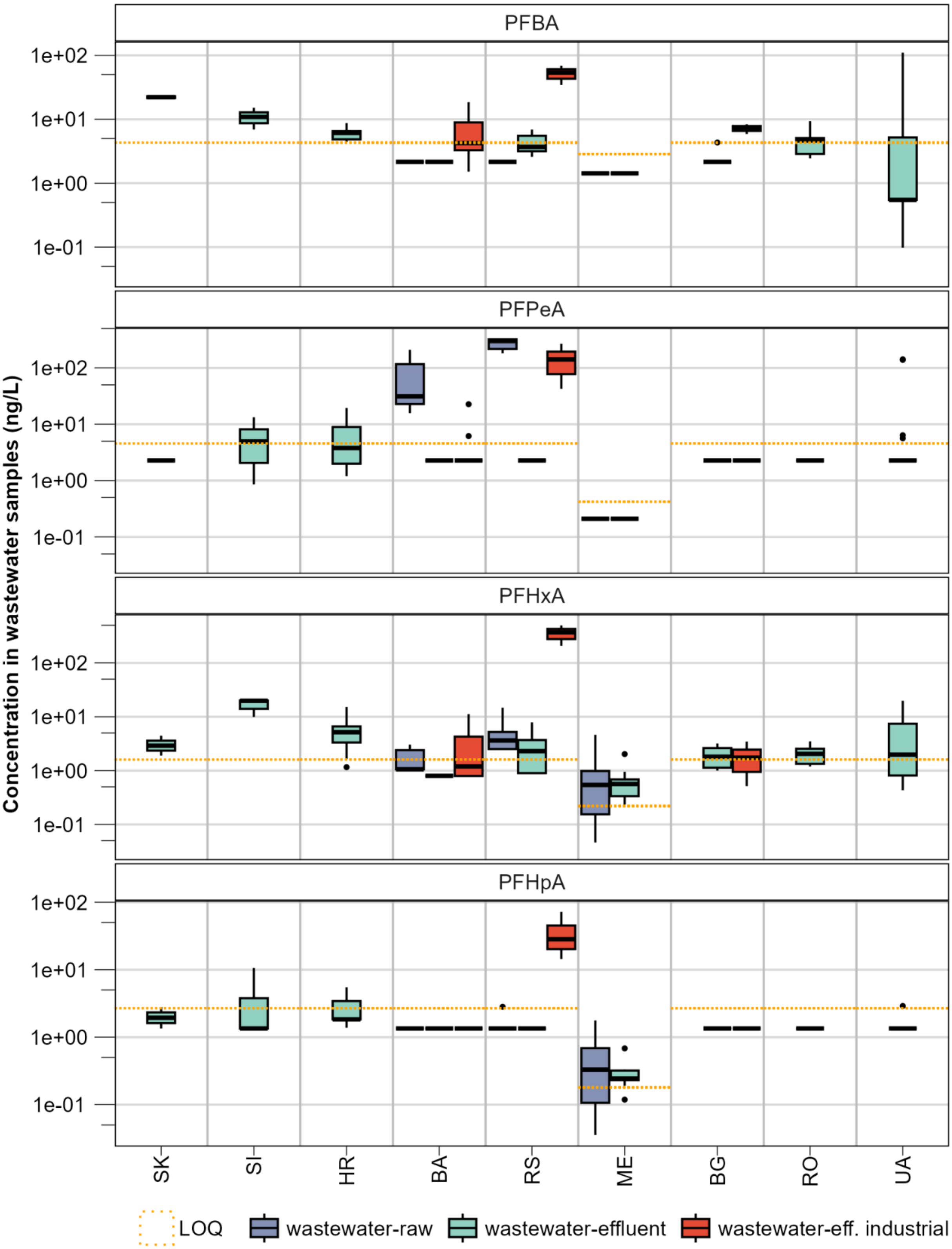


Figure 25: Distribution of PFAS concentrations measured in wastewater samples of different countries.

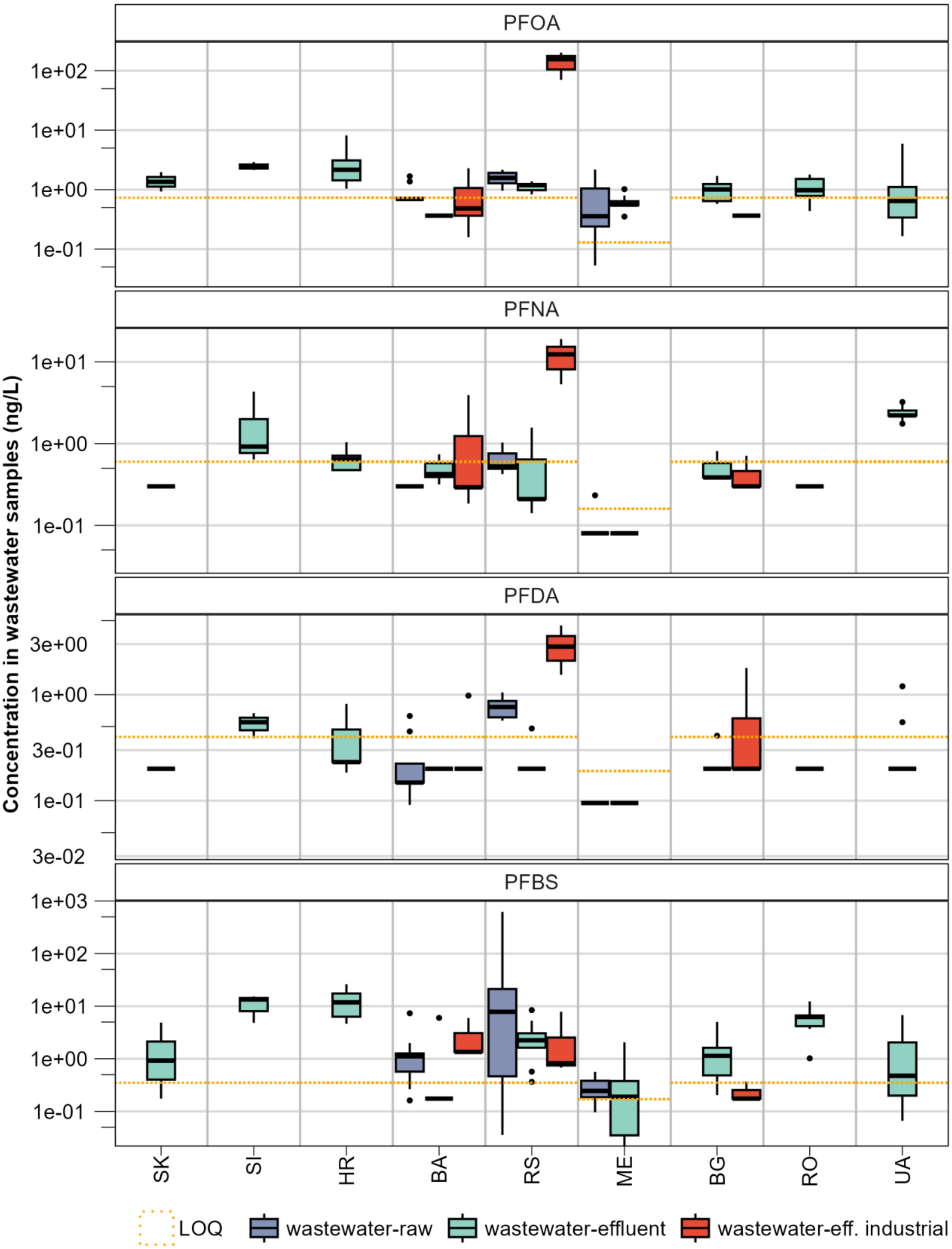


Figure 26: Distribution of PFAS concentrations measured in wastewater samples of different countries.

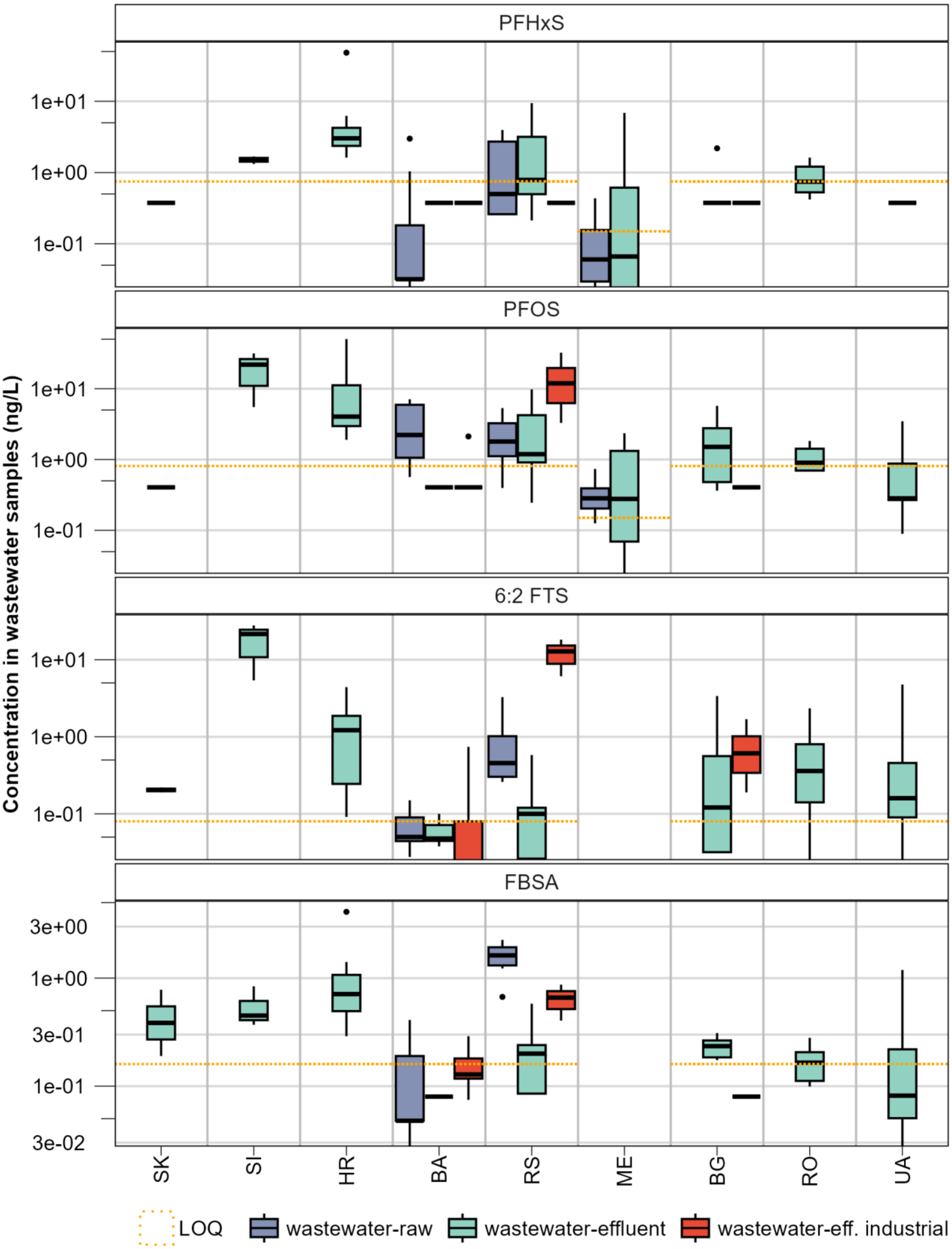


Figure 27: Distribution of PFAS concentrations measured in wastewater samples of different countries.

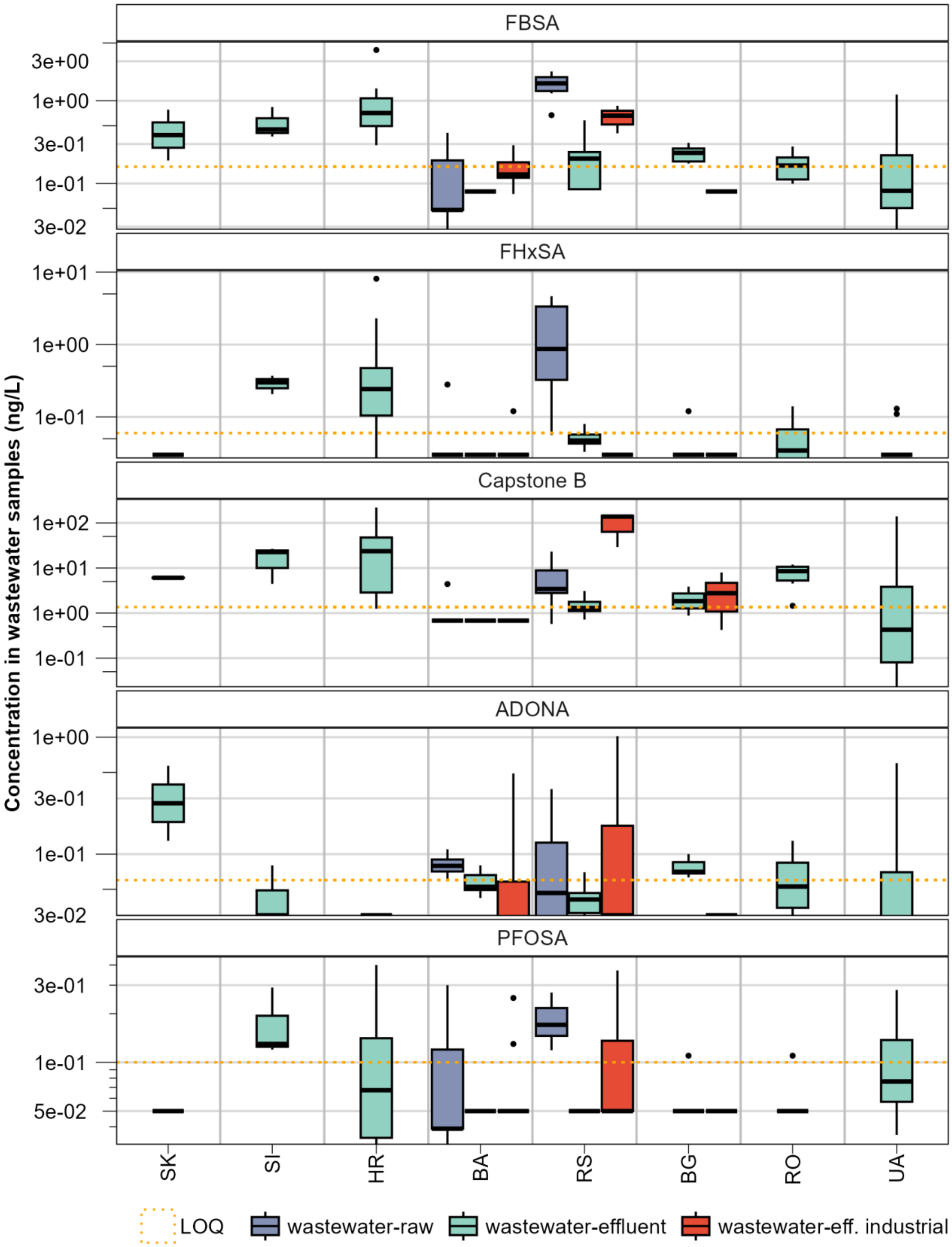


Figure 28: Distribution of PFAS concentrations measured in wastewater samples of different countries.

6.2.3.2 Pharmaceuticals in wastewater samples across countries

Pharmaceutical concentrations in wastewater varied greatly between countries (Figure 29, Figure 30 and Figure 31), with trimethoprim and venlafaxine being exceptions, showing similar median values (within an order of magnitude) across all countries. SK had significantly higher concentrations of metoprolol, diclofenac, citalopram, irbesartan and carbamazepine. Amisulpride concentration ranged from low (BA) to high (SI), with a span of 3.5 orders of magnitude between the median values, with SI showing the highest concentrations. Industrial wastewater effluents vary significantly between countries with RS and BG showing higher concentrations than BA, except for citalopram. The low concentrations of raw wastewater in the ME appear to be a significant underestimation, likely due to a matrix issue during the analysis process. Therefore, in further analyses, we do not want to show underestimations, and these samples are excluded from compartment-wise comparisons.

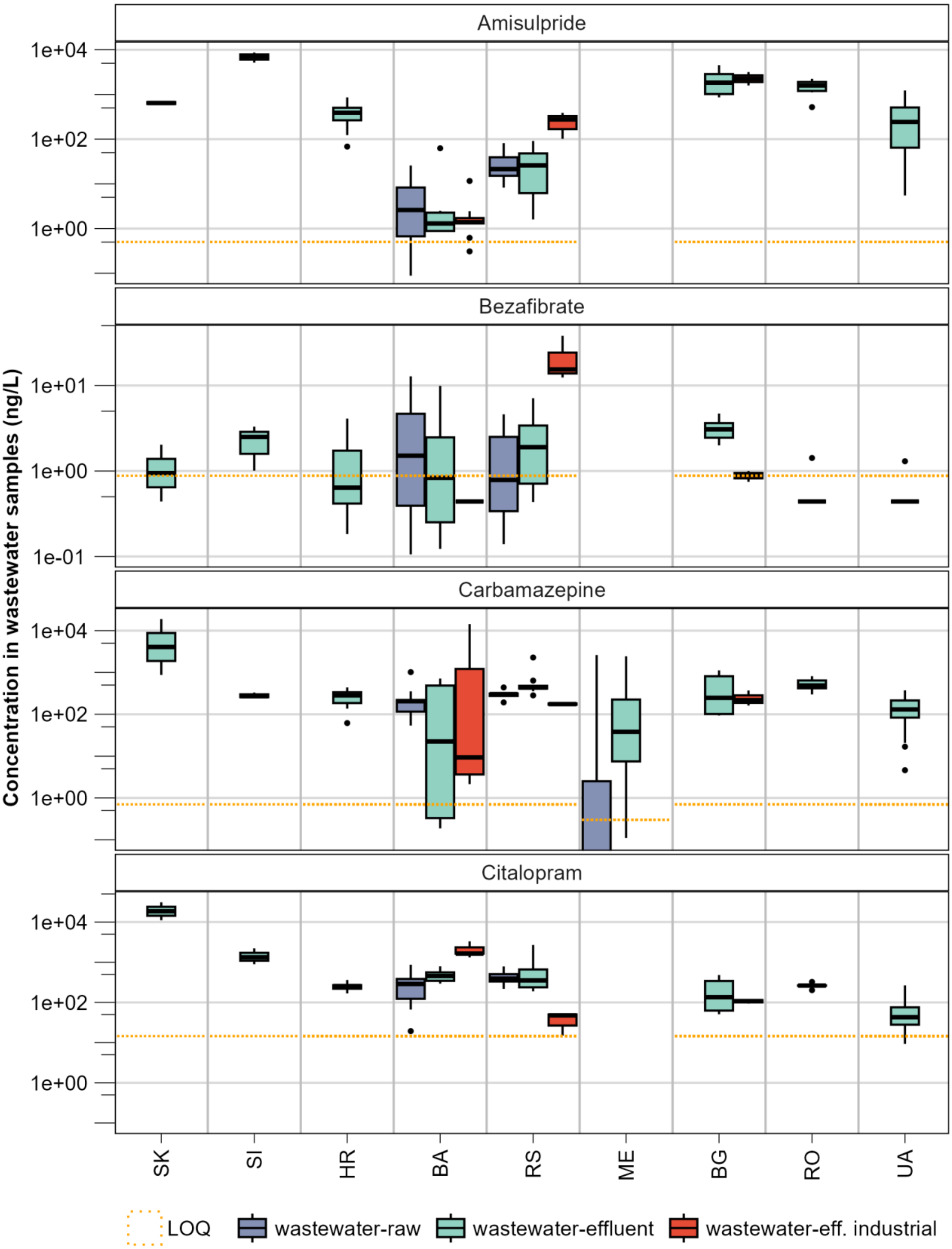


Figure 29: Distribution of pharmaceuticals concentrations measured in wastewater samples of different countries.

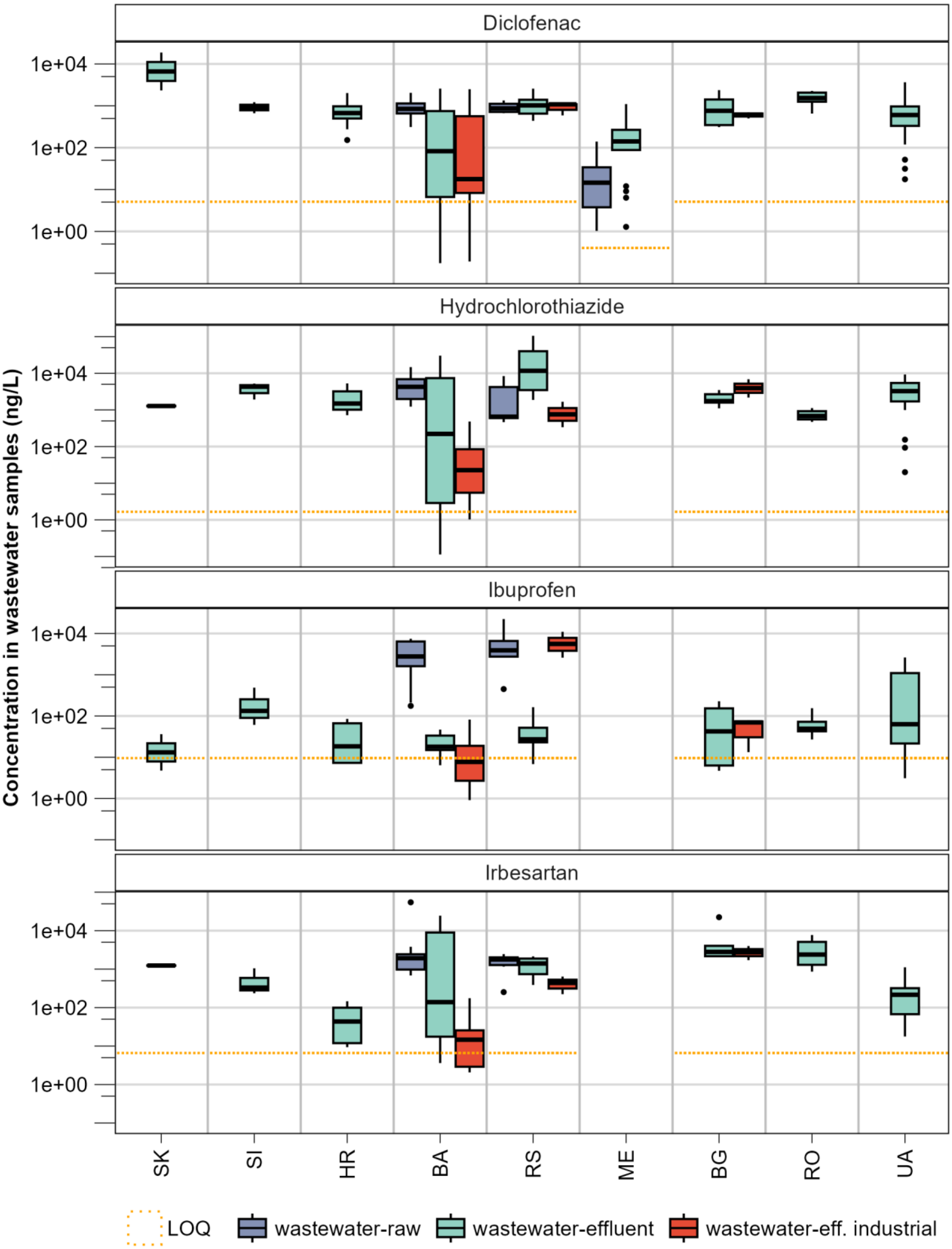


Figure 30: Distribution of pharmaceuticals concentrations measured in wastewater samples of different countries.

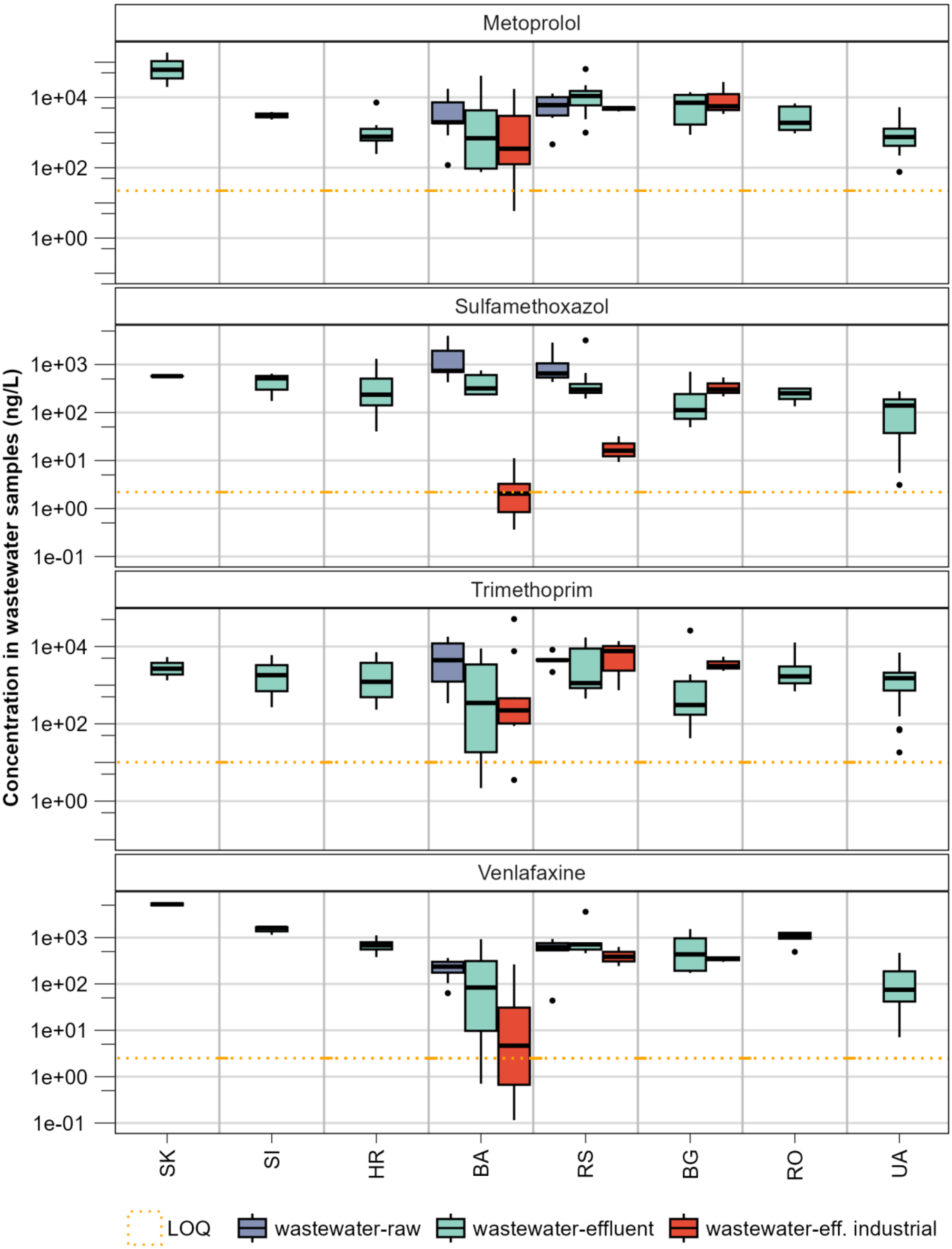


Figure 31: Distribution of pharmaceuticals concentrations measured in wastewater samples of different countries.

6.2.4 PFAS and pharmaceutical concentrations in groundwater samples across countries

PFAS concentrations in groundwater were predominantly below the detection limit, with only occasional outliers. Only short-chain PFCAs (PFBA, PFHxA) and some PFSA (PFBS, PFHxS, PFOS) had a substantial number of values above the LOQ (Figure 32). Country-specific differences were substance-dependent; RS had higher concentrations of PFPeA, PFHpA, PFHxS, PFOS, and some AFFF-related PFAS (6:2 FTS, FBSA, FHxSA), while BA had higher PFBS concentrations. Notably, AFFF-related PFAS were detected only in RS.

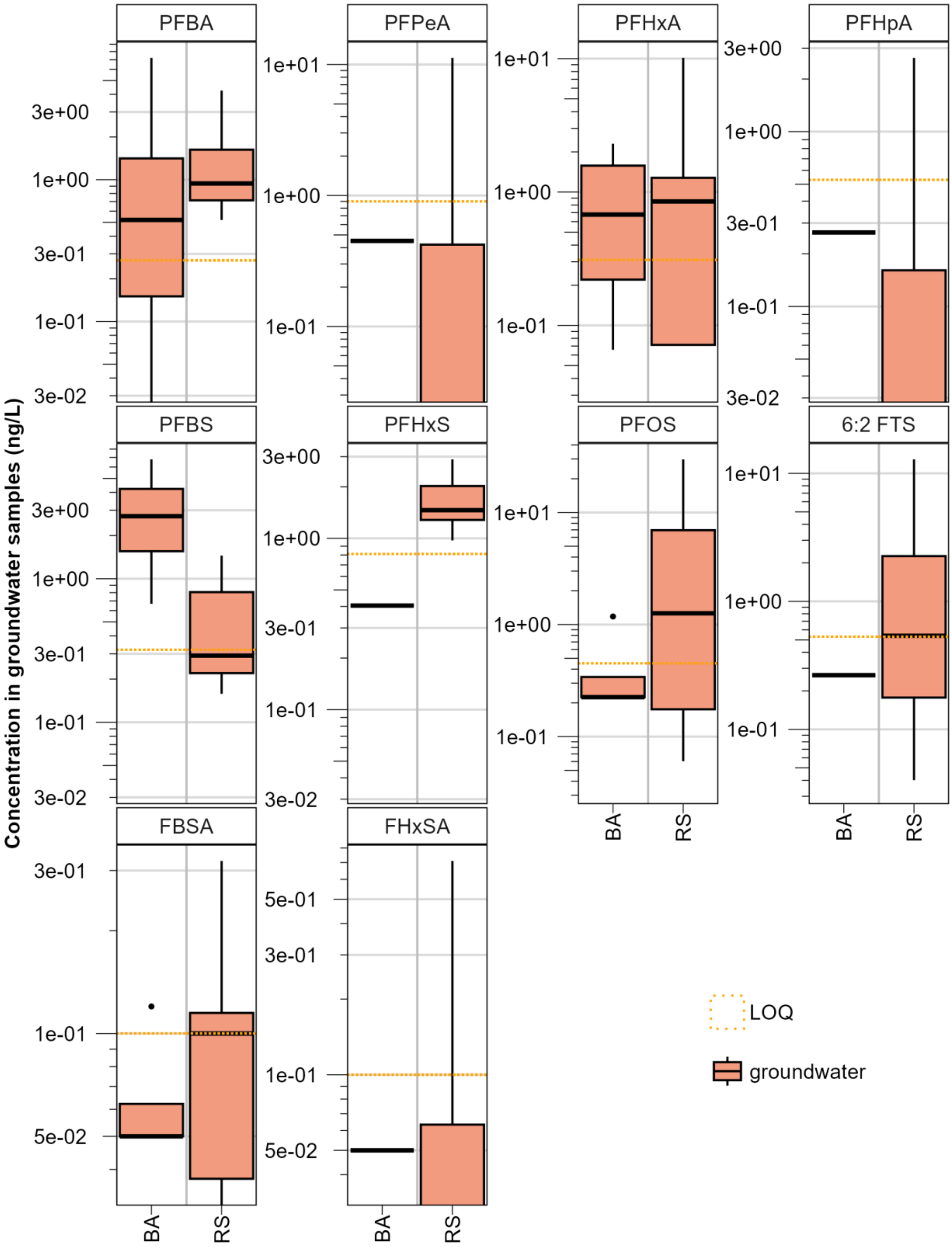


Figure 32: Distribution of concentrations measured for PFAS in groundwater runoff samples in BA and RS.

Pharmaceutical concentrations in groundwater were also mostly below the LOQ, with a few outliers. Only trimethoprim, metoprolol, and amisulpride provided sufficient data for country comparison (Figure 33). Trimethoprim and metoprolol were higher in BA, while amisulpride was higher in RS, though a single outlier from BA represented the maximum observed concentration.

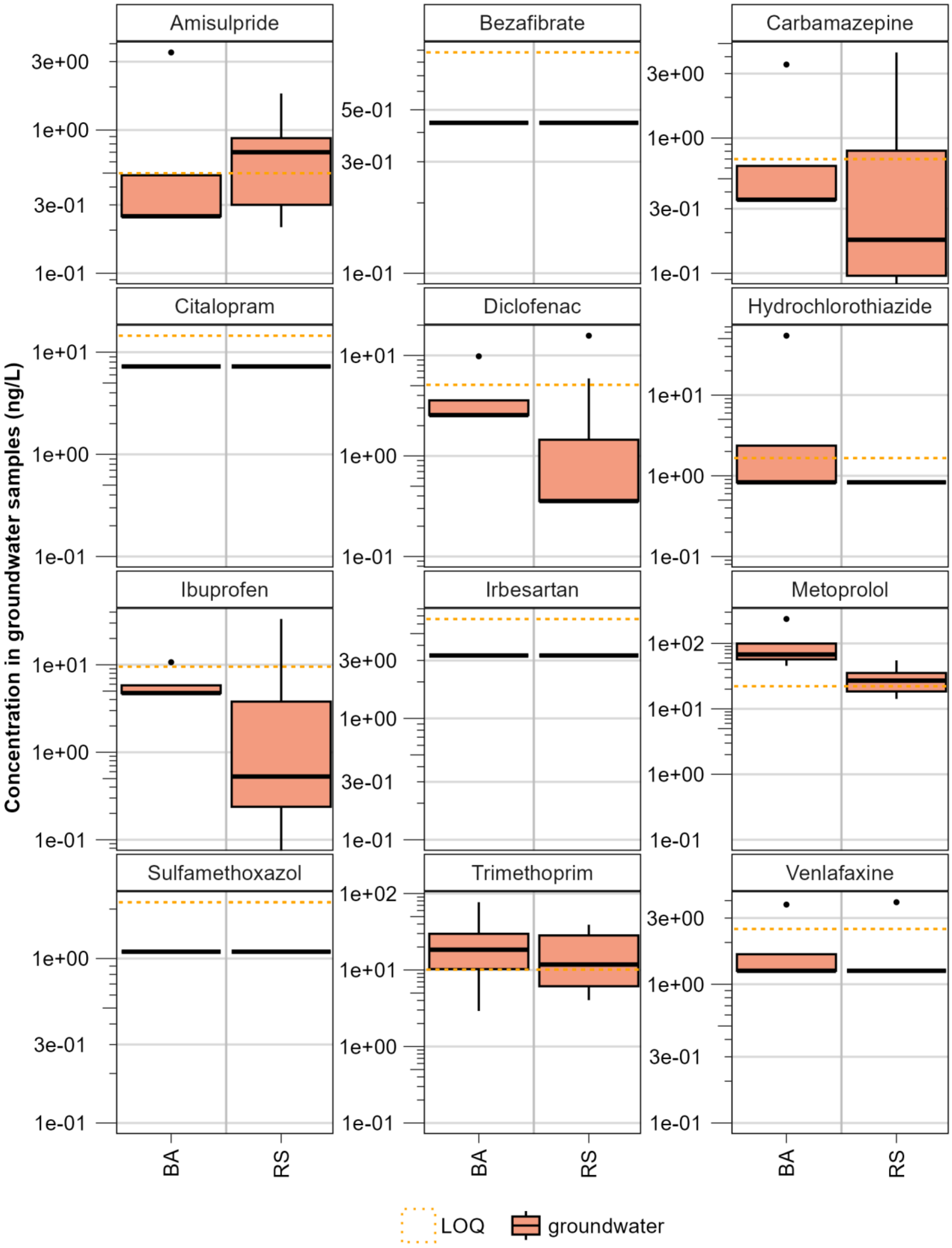


Figure 33: Distribution of pharmaceuticals concentrations measured in groundwater runoff samples in BA and RS.

6.2.5 PFAS and pharmaceutical concentrations in urban stormwater runoff samples across countries

PFAS concentrations in stormwater runoff measured in Austria and Hungary varied over several orders of magnitude (Figure 34 and Figure 35). The combined sewer overflow (CSO) samples were significantly higher than the stormwater samples. PFBS, PFOS and 6:2 FTS were exceptions, with similar concentration levels, while PFBA, PFOSA, N-MeFOSAA, N-EtFOSAA were higher in stormwater. Concentrations of stormwater samples in AT were higher than HU for most substances, except for PFBA, PFBS, PFPeS, and PFHxS.

The concentrations of pharmaceuticals in stormwater runoff varied by one to three orders of magnitude per compound (Figure 36). The combined sewer overflow (CSO) samples were significantly higher than the stormwater samples. Metoprolol was an exception, with similar concentration levels. Direct country comparisons were only feasible for diclofenac and carbamazepine in stormwater samples. For these compounds, AT concentrations were significantly lower than those in Hungary (HU), although outliers in the AT data reached concentrations observed in HU.

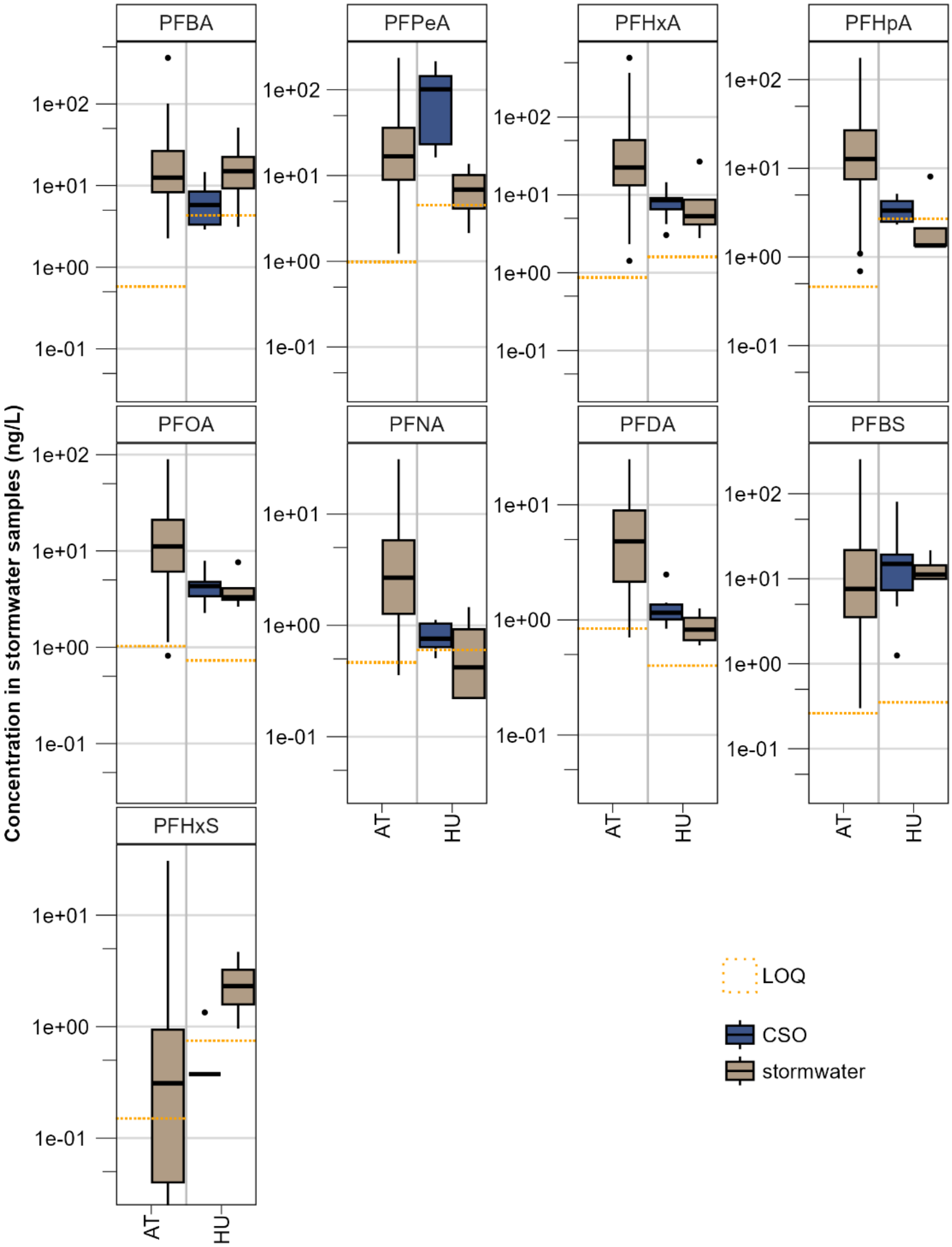


Figure 34: Distribution of PFAS concentrations measured in stormwater runoff samples in AT and HU, part I.

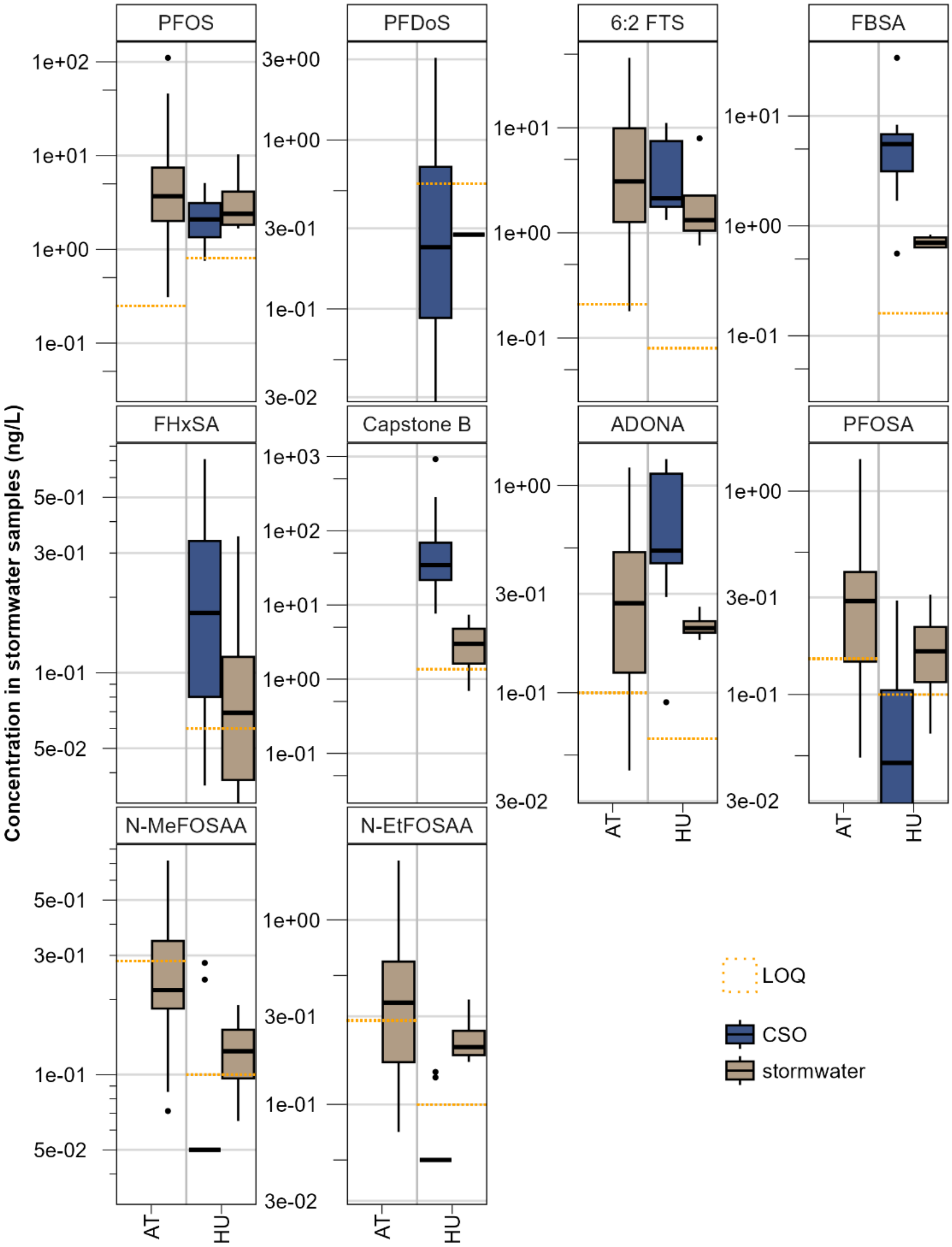


Figure 35: Distribution of PFAS concentrations measured in stormwater runoff samples in AT and HU, part II.

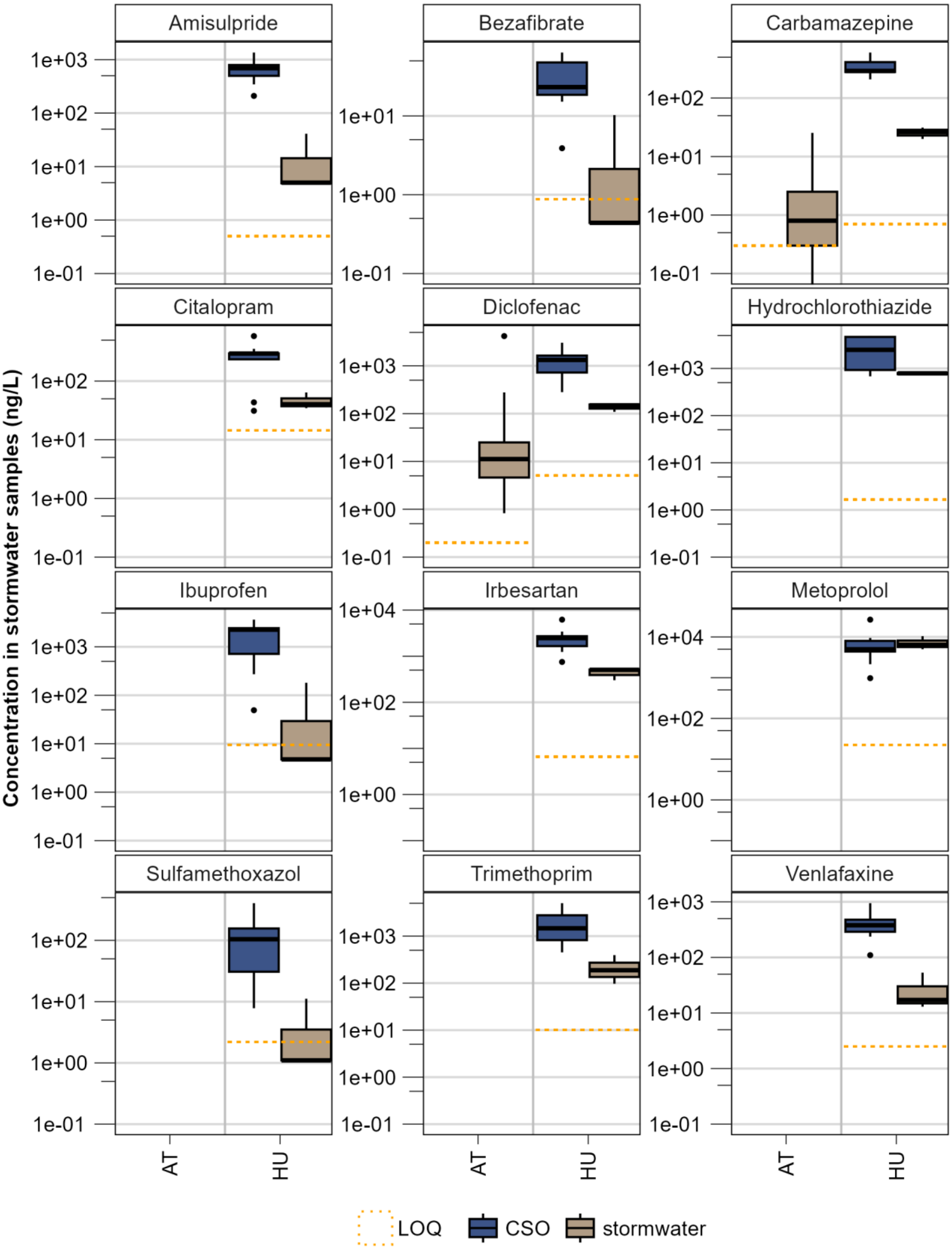


Figure 36: Distribution of pharmaceutical concentrations measured in stormwater runoff samples in AT and HU.

6.2.6 PFAS concentrations across compartments

The ranges of measured concentrations for the most frequently detected PFAS compounds at different types of river sampling sites are presented in Figure 37.

Concentrations for the PFCA group ranged from the LOD (0.1 ng/L) to 100 ng/L. Groundwater and river sites (background and other) generally showed lower concentrations than river hot-spot sites, followed by wastewater and combined sewer overflows (CSO), while the highest concentrations were observed in stormwater. For PFPeA, raw wastewater and CSO had the highest concentrations, while outliers in wastewater effluent and river hot-spot sites reached similar levels. For PFNA and PFDA, the highest median concentrations were found in stormwater, followed by CSO. However, industrial wastewater effluent and river hotspot sites displayed the widest concentration range, despite having lower median values than other categories. For PFHxA, groundwater showed concentrations similar to those at river validation sites and significantly higher levels than river background sites, suggesting possible unaccounted pollution sources. Some river background sites showed PFBA concentrations comparable to other categories, indicating potential unidentified pollution sources. In some samples, PFBA concentrations in rivers were as high as in wastewater effluent, which may be due to insufficient dilution.

The range for the PFSA group spanned from 0.1 ng/L to 100 ng/L. River hotspots and industrial wastewater sites did not show higher concentrations than their comparable groups, indicating that other pollution indicators apply for this group. For PFBS, stormwater and CSO showed the highest concentrations, while some outliers in river sampling sites reached similar levels. Many parameters in this group were either below the LOQ or detected only sporadically. This was particularly true for long-chain PFSA and shorter-chain compounds such as PFPeS and PFHpS. For the frequently detected PFBS, PFHxS, and PFOS, river background sites had significantly lower concentrations than the other two river site categories as well as groundwater.

For the other PFAS substances, concentrations ranged from 0.1 ng/L to 1 ng/L, except for the AFFF-related PFAS, which ranged from 0.1 ng/L to several hundred ng/L, with significant variation in substance-specific LOQs. For ADONA, stormwater and CSO samples showed the highest concentrations, but some river validation sites exhibited similar levels. A similar pattern applies to Capstone B, an AFFF-related PFAS, where some river hot-spot sites showed some of the highest observed concentrations. For FBSA, FHxSA, Capstone B, and ADONA, CSO showed the highest concentrations, while for PFOSA it was stormwater. River background and groundwater were largely unpolluted, but some groundwater sites exhibited elevated concentrations indicating potential contamination. Concentrations for these groups were predominantly below the detection limit (LOD), with few outliers showing concentrations up to an order of magnitude higher than the LOQ. These outliers were typically associated with river (validation or hotspot) or wastewater sites, with the exception of N-EtFOSE and N-MeFOSE, which showed high outliers across many site types.

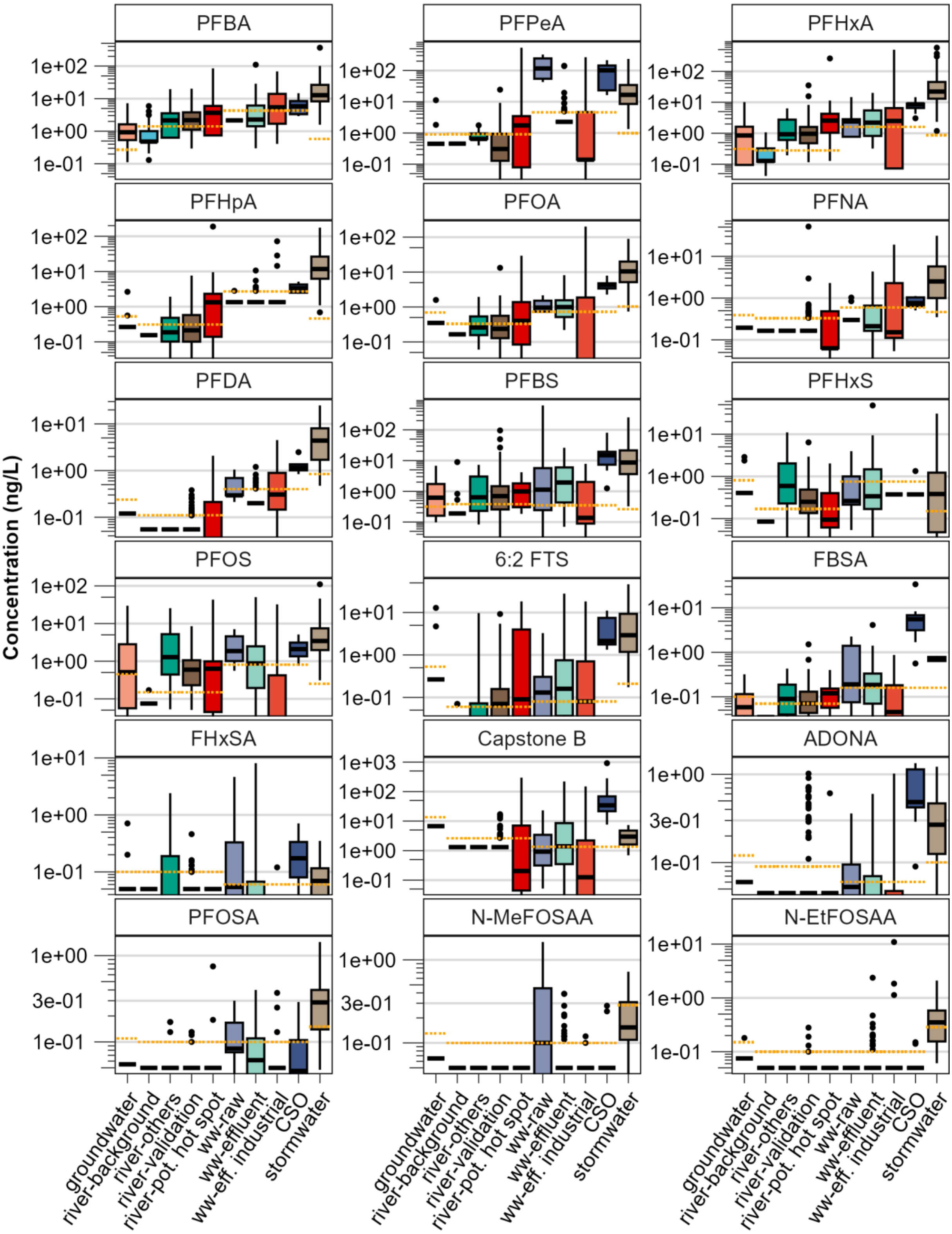


Figure 37: Distribution of PFAS concentrations measured across compartments. Please note that the ME samples are not included.

6.2.7 Pharmaceutical concentrations across compartments

The ranges of measured concentrations for the most pharmaceuticals at different types of compartments are presented in Figure 38. Concentrations of pharmaceuticals ranged from the LOD to 100,000 ng/L. The least contaminated sites were the groundwater and river background samples, followed by the other river categories (validation and others) and stormwater. CSO and wastewater showed the highest concentrations. In some cases, stormwater samples exhibited similar concentrations of substances such as metoprolol, irbesartan and hydrochlorothiazide. Bezafibrate is mostly present in CSO and raw wastewater, as well as in some rivers, probably due to their high proportion of untreated wastewater effluent. However, this is true for almost all substances.

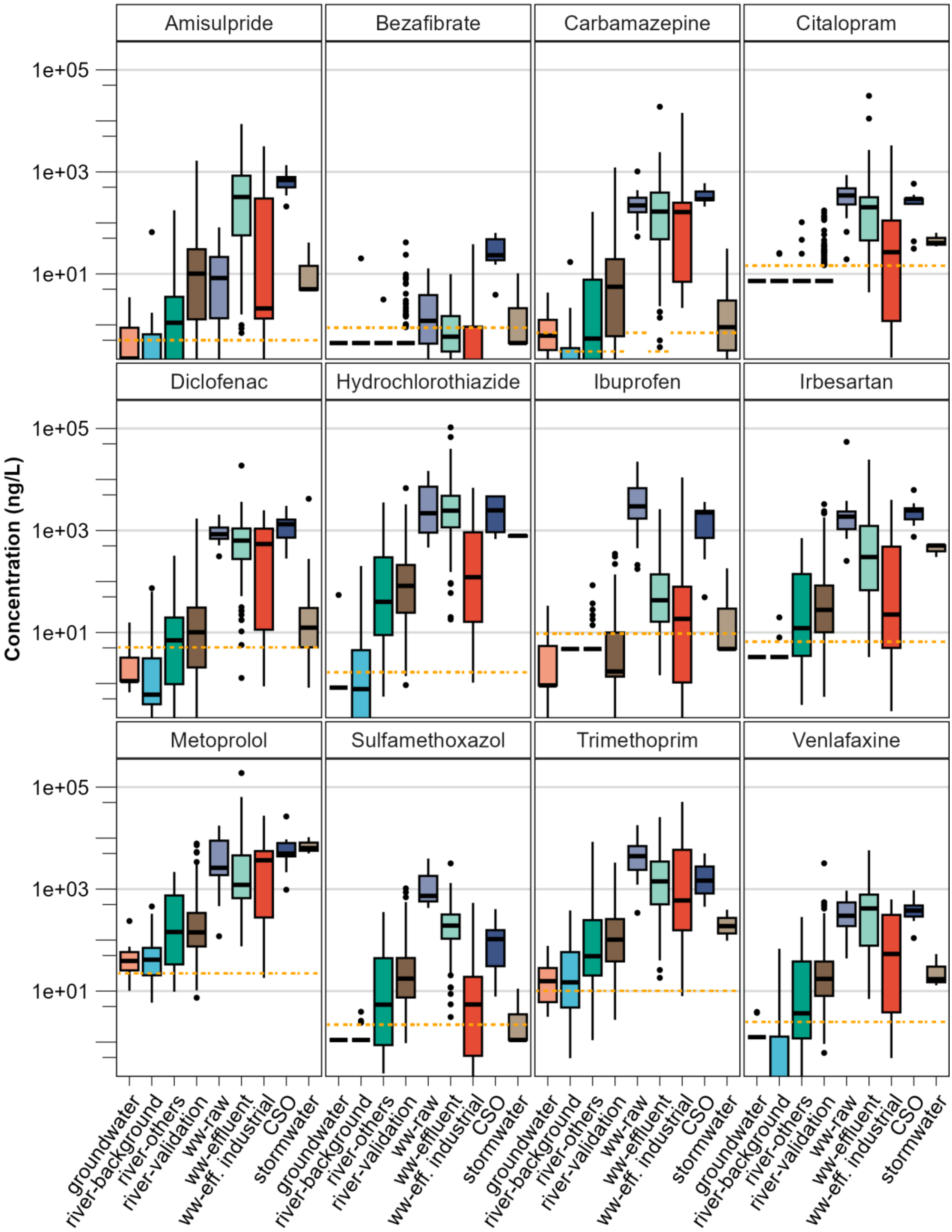


Figure 38: Distribution of pharmaceutical concentrations measured across compartments. Please note that the raw wastewater samples of ME are not included.

7 Conclusions and outlook

The one-year monitoring campaign conducted across 11 countries within the Danube River Basin, including both EU and non-EU states, demonstrated that the feasibility of ***implementation of harmonized and cost-efficient monitoring strategies at the DRB wide level. The results obtained fill crucial information gaps and provide a highly valuable data basis for supporting for supporting the implementation and validation of the MoRE pathway-oriented emission model and for evaluating and comparing the level of contamination, and different profiles of substance relevance, across compartments and countries.***

The monitoring campaigns revealed that metal concentrations in river waters generally meet the EQS criteria set by the WFD, except for known hotspots associated with industrial, mining, or municipal activities. The metal concentrations measured in the Tethys project are generally consistent with previously reported data on total and dissolved concentrations of Zn, Cu, Ni, Cr, As, Cd, and Pb in river waters from the Sava and Evrotas rivers. They are also comparable to dissolved metal concentrations reported for rivers within the Danube catchment. A comparison of the results from the Danube Hazard m^{3}c and Tethys projects shows that the maximum concentrations of elements, both total and in the soluble fraction, are significantly higher at the sites analysed in the Tethys project. This is primarily due to the inclusion of highly contaminated sites in the monitoring scope, particularly the Mjedenički Stream and Rudnica River in Montenegro, as well as the Borska River in Serbia. Similarly, elevated concentrations of Zn and Cu were detected in the Danube Hazard m^{3}c project at the mining area along the Cisla River in Romania. In contrast, the median concentrations, which minimize the influence of extreme values, are similar between the Danube Hazard m^{3}c and Tethys datasets. This suggests that the hotspots at sampling sites in the Tethys project are significant contributors to the deterioration of river water quality, particularly in Montenegro and Serbia, with lesser effect in Bosnia and Herzegovina.

To support the understanding of element transport in river water and for modelling purposes, it is essential to determine both ***total and dissolved element concentrations****. Such measurements have already been conducted in several projects (GLOBAQUA, Danube Hazard m^{3}c, StraMoS, and Hungarian–Slovenian bilateral projects). We recommend that national environmental agencies adopt this approach, even though the WFD currently considers only dissolved element concentrations.*

Wastewater treatment in both EU and non-EU countries is largely effective with respect to metals, as discharges from treatment plants do not exceed levels that would endanger the environment or human health. They also meet the objectives of EU water legislation, which requires effective treatment of urban wastewater to prevent adverse impacts on receiving waters. In areas where wastewater is discharged directly into streams and rivers without prior treatment, the chemical and ecological status of water bodies is noticeably poorer due to elevated metal concentrations. This is also evident at sampling sites from the Danube Hazard m^{3}c project in the mining area along the Cisla River in Romania, where wastewater from mining processing was discharged directly into the river untreated. Insufficient wastewater treatment also directly contributes to elevated metal concentrations and reduced groundwater quality at the locations studied in Serbia and Bosnia and Herzegovina.

The results from the monitoring campaigns for PFAS and pharmaceuticals revealed significant variability across four investigated water compartments—river water, wastewater, groundwater, and urban stormwater runoff—and across countries. Stormwater, CSO and wastewater exhibit the highest detection rates and concentrations, while the selected groundwater sites had the lowest levels. PFAS contamination patterns were complex and compound-specific: long-chain PFAS compounds were rarely detected, whereas short-chain PFAS (e.g., PFBS, BFBA and PFHxA) and AFFF-related PFAS were more frequently found, particularly in wastewater, CSO and stormwater. Country-specific differences were observed, with some countries (e.g., Serbia and Slovenia for wastewater, and Hungary for river water) showing higher contamination levels. The findings highlight CSO and stormwater runoff as a potentially significant contributor to PFAS and pharmaceutical contamination, while wastewater is confirmed as pathway with a significant role—particularly for persistent compounds. Groundwater was largely uncontaminated, though occasional outliers indicated localized pollution. Additionally, significant site-specific variability was observed, with "hot-spot" and "validation" sites typically more contaminated than "background" locations. These results underscore the need for targeted monitoring and mitigation strategies to address these emerging pollutants in different water environments and locations.

*The implementation of harmonized and cost-efficient monitoring strategies for HS emissions and pollution inventories, as demonstrated in the Tethys project, also highlighted the need for effective treatment **of wastewater** from municipal, industrial, and mining wastewater, as well as runoff, **in order to maintain river and groundwater quality consistent with the requirements for good chemical and ecological status**.*

8 References

D1.1.1: Protocol for Sampling, Storage, and Transport of Samples. June, 2024.

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy. Official Journal of the European Union, L 348, 84-97. https://eur-lex.europa.eu/eli/dir/2008/105/oj. Accessed December 27, 2025.

Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy. Official Journal of the European Union, 12 Aug. 2013, L 226/1-17. EUR-Lex, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32013L0039. Accessed December 27, 2025.

Directive (EU) 2024/3019 of the European Parliament and of the Council of 27 November 2024 Concerning Urban Wastewater Treatment. Official Journal of the European Union, 27 Nov. 2024. EUR-Lex, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32024L3019. Accessed December 27, 2025.

European Communities Environmental Objectives (Surface Waters), 2009. Regulations S.I. No. 272/2009. https://www.irishstatutebook.ie/eli/2009/si/272/made/en/pdf.

EU (2012). Technical guidance on the preparation of an inventory of emissions, discharges and losses of priority and priority hazardous substances. Guidance document No. 28. https://legacy.emissieregistratie.nl/erpubliek/documenten/06%20Water/02%20Achtergrondrapporten/WFD%20guidance%20on%20emission%20inventories.pdf. Accessed December 27, 2025.

ISO 5667-3:2018 Water quality — Sampling — Part 3: Preservation and handling of water samples. https://standards.iteh.ai/catalog/standards/sist/c196ec4b-72ef-4cac-a087-e44ae7787139/sist-en-iso-5667-3-2018

Kittlaus, S., Clara, M., van Gils, J., Gabriel, O., Broer, M. B., Hochedlinger, G., ... & Zoboli, O. (2022). Coupling a pathway-oriented approach with tailor-made monitoring as key to well-performing regionalized modelling of PFAS emissions and river concentrations. Science of The Total Environment, 849, 157764

Liška, I., Wagner, F., Sengl, M., Deutsch, K., Slobodník, J., 2015. ICPDR (International Commission for the Protection of the Danube River) Joint Danube Survey 3. A Comprehensive Analysis of Danube Water Quality, Final Scientific report of the International Commission for the protection of the Danube River. Vienna, Austria. p. 231–239. https://www.icpdr.org/sites/default/files/nodes/documents/jds3_final_scientific_report.pdf. Accessed December 27, 2025.

Lučić, M., Mikac, N., Vdović, N., Bačić, N., Nava, V., Vidmar, J., Milačič, R., 2022. Spatial and temporal variability and sources of dissolved trace elements in the Sava River (Slovenia, Croatia). Environ. Sci. Pollut. Res., 29, 31734–31748. https://doi.org/10.1007/s11356-022-20684-3.

Milačič, R., Zuliani, T., Vidmar, J., Oprčkal, P., Ščančar, J., 2017. Potentially toxic elements in water and sediments of the Sava River under extreme flow events. Sci. Total Environ. 605–606, 894–905. http://dx.doi.org/10.1016/j.scitotenv.2017.06.260.

Milačič, R., Zuliani, T., Vidmar, J., Bergant, M., Kalogianni, E., Smeti, E., Skoulikidis, N., Ščančar, J., 2019. Potentially toxic elements in water, sediments and fish of the Evrotas River under variable water discharges. Sci. Total Environ. 648, 1087–1096. https://doi.org/10.1016/j.scitotenv.2018.08.123.

Milačič, R., Marković, K., Marković, S., Ščančar, J., Jolánkai, Z., Clement, A., Musa, I., Krisztián Kardos, M., Zoboli, O., Zessner, M., 2023. Changes in concentrations of potentially toxic elements during storage of hard river water samples at low temperatures using different sample preservation procedures. J. Soils Sediments 23, 4173–4186. https://doi.org/10.1007/s11368-023-03625-5.

Niampradit, S., Kiangkoo, N., Mingkhwan, R., Kliengchuay, W., Worakhunpiset, S., Limpananont, Y., Hongsibsong, S., Inthorn, D., Tantrakarnapa, K., 2024. Occurrence, distribution, and ecological risk assessment of heavy metals in Chao Phraya River, Thailand. Sci. Rep. 14, 8366. https://doi.org/10.1038/s41598-024-59133-0.

Official Gazette of the Republic of Slovenia (2012). Regulation on the emission of substances and heat from the discharge of wastewater into water and public sewers. Official Gazette of the Republic of Slovenia, 64/2012, p. 6392. (In Slovenian language). https://www.uradni-list.si/_pdf/2012/Ur/u2012064.pdf. Accessed December 27, 2025.

Official Journal of the European Communities, 2000. Directive 2000/60/EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy L 327/1. https://eur-lex.europa.eu/eli/dir/2000/60/2014-11-20. Accessed December 27, 2025.

Olías, M., Cánovas, C.R., Macías, F., Basallote, M.D., Nieto, J.M., 2020. The Evolution of Pollutant Concentrations in a river severely affected by acid mine drainage: Río Tinto (SW Spain). Minerals, 10, 598. DOI:10.3390/min10070598.

O1.1: Testing and demonstration of harmonized and cost-efficient monitoring strategies in non-EU countries and in new critical compartments as a basis for HS emissions and pollution inventories. December, 2025.

Proposal for a Directive of the European Parliament and of the Council amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, Directive 2006/118/EC on the protection of groundwater against pollution and deterioration and Directive 2008/105/EC on environmental quality standards in the field of water policy Mandate for negotiations with the European Parliament (2024). https://eur-lex.europa.eu/procedure/EN/2022_344. Accessed December 27, 2025.

Wang, Z., Walker, G. W., Muir, D. C., & Nagatani-Yoshida, K. (2020). Toward a global understanding of chemical pollution: a first comprehensive analysis of national and regional chemical inventories. Environmental science & technology, 54(5), 2575-2584.

Weisner, O., Arle, J., Liebmann, L., Link, M., Schäfer, R. B., Schneeweiss, A., ... & Liess, M. (2022) Three reasons why the Water Framework Directive (WFD) fails to identify pesticide risks. Water Research, 208, 117848.