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How reliable are estimates of trace contaminants in rivers based on monthly grab samples?

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Abstract

Background Water quality assessment must rely on representative samples, but obtaining them is increasingly challenging given the growing number and diversity of trace contaminants emitted into water bodies. This study investigates whether and to what extent monthly grab sampling (GS), widely used in official monitoring programmes, provides reliable and accurate estimates of annual mean and maximum concentrations, and of annual riverine loads. Through a one-year systematic survey in two rivers using three sampling techniques in parallel, we evaluate low-frequency GS against time-proportional composite (TPC) and flow-proportional composite (FPC) sampling. The scope of 450 contaminants encompasses potentially toxic elements (PTE), pharmaceuticals, biocides, pesticides and PFAS, covering a broad diversity of emission patterns and environmental fate.

Results For dissolved PTEs and pharmaceuticals, monthly GS delivered approximately correct annual average concentrations, but potential underestimation and overestimation were also observed. Contaminants with seasonal patterns or those emitted during short-term events, such as many pesticides and biocides, PFAS and total PTEs, were not adequately depicted by low-frequency GS, leading to varying degrees of underestimation and seldom also to overestimation. This applies to average annual concentrations but particularly to loads. Integrated composite sampling, especially flow-proportional, performs significantly better for such contaminants. Worthy of attention are cases of low and highly variable concentrations, such as ibuprofen, lindane and PFNA in this study. While integrated composite samples clearly demonstrated their non-negligible presence, monthly GS failed to detect them.

Conclusion The widely applied monitoring approach relying on monthly GS is only sufficiently reliable for contaminants being emitted fairly constantly and transported primarily in the dissolved phase. Even then, its good performance is mostly limited to assessing average concentrations and thus chronic exposure, while integrated composite sampling can significantly improve the accuracy of load calculations. For contaminants with variable and dynamic concentration patterns, FPC sampling performs considerably better, especially in terms of load calculations, followed by TPC sampling. However, the latter is simpler to implement. GS-based underestimations pose a significant risk of incorrectly assessing compliance with environmental quality standards if the concentration level in rivers is not very far below or above the thresholds, as was often the case in our study area.

Keywords Diffuse emissions, Micropollutants, Monitoring, Pesticides, Pharmaceuticals, PFAS, Priority substances, PTE, Water quality

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Background

Water quality monitoring is the primary instrument for assessing the physical, chemical and ecological status of rivers, as well as for identifying the main anthropogenic pressures and environmental changes impacting water resources and freshwater ecosystems. To achieve these overarching goals, the information provided by monitoring must meet several specific objectives, such as assessing compliance with environmental quality standards, identifying temporal trends, and estimating riverine loads. Loads in turn provide the essential basis for assessing the transboundary transport of substances via waterways, quantifying their transfer to seas and lakes, and calibrating or validating emissions and water quality models. For nutrients and other common chemical analytes, the suitability of different monitoring strategies, particularly in terms of their temporal resolution, has been widely discussed in the literature in relation to different specific objectives and varying emission and transport dynamics. A low sampling frequency, especially if it does not encompass high-flow conditions, can lead to severe underestimates of suspended solids and total phosphorus loads [11, 38]. It was also shown that it could potentially lead to an underestimation of the loads of other nutrients that are partially mobilised during storm events (K^+ and NO^{3-}), and to an overestimation of the loads of solutes that are diluted during such events (e.g., SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, Cl^-) [49]. Regarding the suitability of monitoring strategies for assessing compliance with regulatory values, such as the ecological status classification scheme of the Water Framework Directive (WFD, 2000/60/EEC), various studies provide evidence of the influence of sampling frequency. Skeffington et al. [43] demonstrated that random sampling effects when monitoring key parameters (dissolved phosphorus, dissolved oxygen, pH, and water temperature) on a monthly basis, could lead to the misclassification of water bodies into up to four WFD classes (95 % confidence) in extreme cases. However, it is important to emphasise that the observed effect on WFD classification was highly dependent on how close the range of measured concentrations was to the class boundaries. Similar to that of Skeffington et al. [43], Benisch et al. [2] compared high-resolution data obtained from online monitoring with data from monthly sampling and concluded that the latter is not sufficiently accurate for determinants with pronounced temporal patterns and for which maximum or minimum concentrations are regulated. However, for analytes with low temporal variability and for which mean values are defined in regulations, such as chloride and nitrate-nitrogen, no significant benefits were identified from increasing the temporal resolution of sampling.

In comparison with nutrients and standard physicochemical parameters, trace organic and inorganic contaminants present an added challenge for monitoring. These include not only the higher financial burden associated with chemical analyses but also the complex physicochemical properties that dictate their environmental behaviour. The selection of a sampling method must also account for the contaminant's sorption potential, which is commonly described by the organic carbon partition coefficient (K_{oc}). A practical threshold was established by Schaar et al. [42], with a log K_{oc} < 3.3 indicating low sorption. Critically, these authors also found that pharmaceuticals consistently exhibit poor sorption behaviour, regardless of their K_{oc} values. Therefore, a thorough understanding of this physicochemical property is essential for selecting a suitable sampling strategy.

Within the European Union, the WFD's Annex V stipulates a monthly sampling frequency for contaminants defined as priority substances in the Environmental Quality Standard Directive (2013/39/EU) [9] and a quarterly sampling frequency for other pollutants. The guidance document on surface chemical monitoring, elaborated within the Common Implementation Strategy for the WFD [8], specifies that on the one hand, a reduced sampling frequency or even no monitoring could be justified under certain circumstances, and on the other hand, more frequent sampling could be necessary, e.g. for load estimation, for trend detection or to increase the level of confidence and precision in the status assessment. The actual implementation of chemical monitoring in surface waters across European countries varies significantly, in terms of chemical substance spectra, sampling frequency, temporal continuity and spatial network density [57]. Through their comparative assessment, Wolfram et al. [57] demonstrated the correlation between higher monitoring quality, in terms of higher values for the four aspects mentioned above, and the success in detecting contaminants. They therefor highlighted the risk of ecological impairments being overlooked due to insufficient monitoring efforts, particularly regarding pesticides. In general, it is primarily for this group of pollutants that conventional monitoring based on monthly grab samples has been questioned and criticised. A recent large study in Germany, focusing on small agricultural catchments, indicated that the WFD-compliant monitoring leads to a significant overestimation of the chemical status of water bodies and to an underestimation of the contribution of pesticides to the ecological status [52]. The study identified conventional monthly sampling, which mostly fails to cover storm events, as one of the main reasons for the inadequate assessment of pesticide exposure in surface water systems under the WFD. Similar conclusions were reached by Chow et al. [6] in their review of long-term pesticide monitoring studies, which highlighted the need to consider interannual variability in exposure in monitoring programmes, mainly due to seasonality of application and hydrological conditions driving transport processes. Such considerations have led some countries to adapt their monitoring programmes for pesticides, pursuing a compromise between time resolution and length of monitoring period. For example, Sweden and Norway have adopted an approach that relies on weekly or biweekly composite samples from April to October [44], while Switzerland implemented standard biweekly composite samples throughout the year [7]. In this respect, the findings of Herrmann et al. [20] provide novel insights into the complex patterns of pesticides emissions and fate in surface waters, which give rise to the question of whether limiting monitoring to the growing season is an adequate approach, and underscore the necessity of expanding sampling frequency. They found that fungicides manifested predominantly in intermittent patterns, whereas some exhibited a tendency towards (pseudo)-persistence. Neonicotinoids and legacy pesticides demonstrated a permanent occurrence, with detection persisting for several months after application.

Pesticides represent just one group of the vast array of synthetic substances being released into the environment and eventually reaching water bodies. Current estimates place the number of chemicals and mixtures of chemicals that have been registered for production and use at over 350,000 [50]. This poses a significant challenge for effective water quality monitoring due to the enormous heterogeneity of sources, emission pathways, and environmental fate. Wittmer et al. [56] investigated the adequacy of various sampling strategies with a particular focus on diffuse emissions and identified the use of time-integrated composite samples as the most suitable compromise solution for depicting chronic exposure. To accurately depict acute exposure and estimate annual loads, however, they recommend utilising either flow-proportional composite samples or high-frequency sampling during storm events. Point emissions from municipal and industrial wastewater treatment plants (WWTP) can also present patterns that are challenging for monitoring. In this respect, Ulrich et al. [48] demonstrated the risk of per- and polyfluoroalkyl substances (PFAS) going undetected in a highly impacted river via conventional grab sampling, likely due to the presence of industrial batch operations resulting in discontinuous emissions. The number and diversity of trace contaminants with obligatory monitoring for the assessment of chemical and ecological status in the EU are currently very limited. The current proposal for a new Environmental Quality Standards Directive [10] would significantly extend the list, and heterogeneity of substances. Furthermore, the growing number of chemicals is expected to exert major pressure on surface waters systems [14]. This will lead to the necessity of expanding monitoring programmes in specific cases or basins. In this increasingly complex context, water management authorities and environmental technical agencies require robust evidence and support to select fit-for-purpose monitoring programmes.

The present study contributes to this goal by investigating whether and to what extent a monthly grab sampling approach results in significant deviations from actual values when estimating annual mean and maximum concentrations, as well as annual riverine loads, for a wide range of inorganic and organic trace contaminants. This question was systematically addressed by conducting a one-year survey based on three sampling techniques applied in parallel: monthly grab sampling, biweekly time-proportional, and biweekly flow-proportional composite sampling. The monitoring was carried out at two sites located in the catchment area of the River Wulka in eastern Austria. The site on the Wulka is distinguished by a catchment area that exhibits a pronounced agricultural character, but it is also subject to significant influence from discharges originating from municipal WWTPs, accounting for approximately one-third of the annual mean water flow. The catchment area of the second station in the Nodbach, a tributary to the Wulka, is also primarily influenced by agriculture; however, it does not receive any WWTP effluent. A significant strength of the study is in the inclusion of several groups of contaminants, selected to represent a broad spectrum of emission sources, pathways, fate, and transport behaviours at the catchment scale and in river systems. The scope of the contaminants analysed (450 in total) encompasses the following groups: (i) potentially toxic elements (PTE), analysed both in their total and dissolved fractions, the total values being representative of predominant particle-bound and erosion-driven transport; (ii) pharmaceuticals from human medicine, which are predominantly emitted via municipal WWTPs; (iii) pesticides and biocides, primarily transferred into water bodies via diffuse emission pathways and often characterised by a highly dynamic and partly seasonal transport pattern; and (iv) PFAS, representatives of industrial chemicals with a very broad spectrum of emission sources and complex environmental behaviour. Thanks to its systematic design and broad analytical scope, this study provides highly representative results and has clear added value in that its findings can be extended to additional contaminants with similar emission sources and environmental behaviour.

Methods

Case study area

Situated in south-eastern Austria, the Wulka catchment covers an area of approximately 400 km^2. Its topography is predominantly flat, with mixed land use primarily dedicated to arable land. The main river, the Wulka, flows from south-west to north-east, ultimately discharging into Lake Neusiedl, which is Austria's second biggest lake (see Fig. 1). The Wulka's discharge, with a long-term mean of 1.12 m^3 s^{-1} (1961–2024), consists of municipal wastewater treatment effluents up to 36 % in average due to a relatively low long-term precipitation level (695 mm y^{-1}). It also exhibits significant variation of discharge between high and low flow conditions. This hydrological variability critically influences pollutant transport, as the proportion of wastewater-derived pollutants can rise over 50 % during periods of low flow, which mainly occur during summer month. The Nodbach is a right bank tributary of the Wulka with a catchment area of 76 km^2 and a long-term mean flow of 0.09 m^3 s^{-1} (1992–2024) and, in contrast to the main river, it does not receive any discharge from WWTPs. The SI contains a table outlining the main characteristics (Table SI1).

Monitoring stations

Two monitoring stations with the same technical features were installed at the Nodbach and at the Wulka at the outlet of the catchment. Each station consisted of two autosamplers, connected to sensors in the water for the inline continuous measurement of turbidity, conductivity and temperature, a water level sensor, and electronic components for remote control and data transfer of the inline measurements. The autosamplers were 'Endress & Hauser' (E&H) 'Liquistation CSF48' and 'MAXX' 'SP4 S', each equipped with a vacuum pumping system and a 25-litre wide-mouth glass vessel, placed in refrigerated containers to ensure dark and cooled storage during the sampling period. Sampling was carried out through an ethylene propylene diene monomer rubber (EPDM) tube with a 13x19 mm diameter. The sensors consisted of E&H optical turbidity probes 'Turbimax CUS51D' with compressed air cleaning, E&H inductive conductivity and temperature probes 'Indumax CLS50D' and the E&H radar water level probes 'Micropilot FMR10'. Remote inline measurements with one-minute intervals were stored and managed with the data acquisition system 'iTUWmon' [55]. In addition, hydrological measurements from the gauges of the Burgenland Provincial Government situated near the monitoring stations were available.

Sampling, transport and storage of samples

Sampling was conducted over a one-year period (June 2023–June 2024) at two sites. For each 14-day sampling

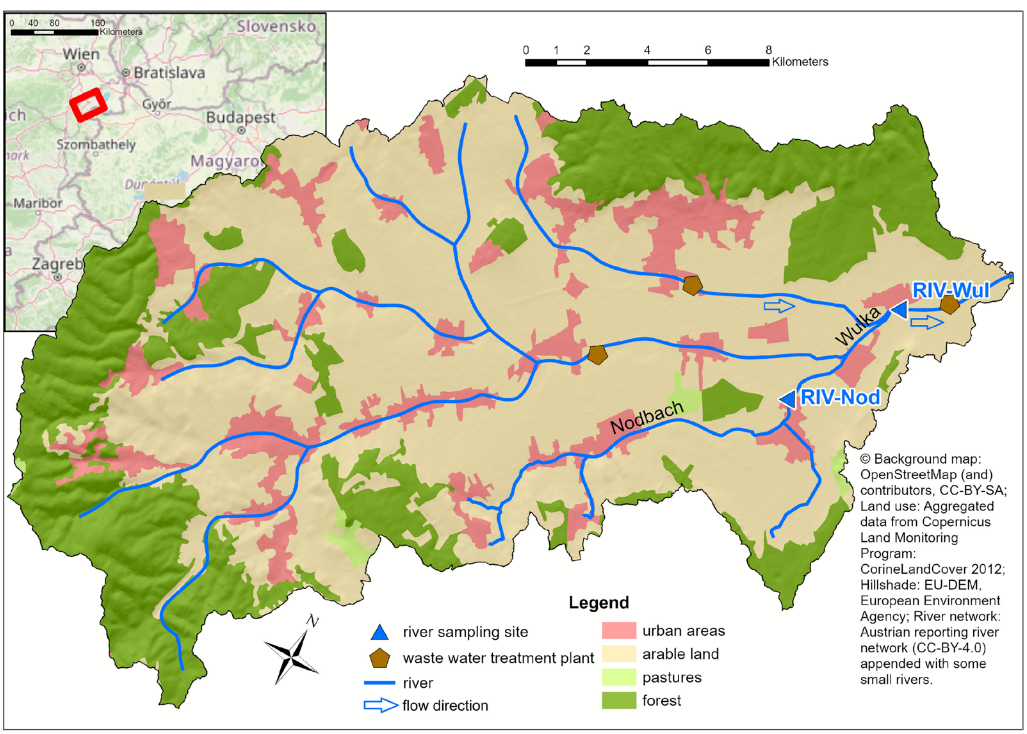

Fig. 1 Map of the Wulka catchment showing land use and sampling locations

cycle, three sampling modes were employed: (1) time-proportional composite (TPC) samples, collected at constant intervals; (2) flow-proportional composite (FPC) samples, collected at a frequency proportional to the river flow; and (3) grab samples (GS), collected manually. A detailed summary of sampling mode is provided in Table SI2.

Immediately after collection, samples were processed for various analyses. Aliquots for pesticide, pharmaceutical, and PFAS analysis were transferred to appropriate containers and stored under refrigeration. Samples for PTE analysis were filtered (0.45 μm) for the dissolved fraction, in accordance with the recommendations of Milačič et al. [33]. All PTE aliquots were stabilized with nitric acid. Samples for PTE, TSS, and water hardness were frozen or refrigerated as required and transported under cooled conditions to certified laboratories for analysis. Detailed protocols for sample preservation, container types, transport logistics, and quality control procedures are provided in the Supporting Information (Section SI1.1).

Chemical analyses

A total of 450 trace contaminants were analysed, encompassing 8 PTE in total and dissolved fractions, 4 pharmaceuticals, 404 pesticides and biocides, and 34 PFAS.

PTE concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). For total concentrations, samples underwent microwave-assisted acid digestion prior to analysis. PFAS were quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) with isotopically labelled internal standards [13]. Pharmaceutical analysis was performed via online solid-phase extraction (SPE) coupled to LC-MS/MS [27]. Pesticides and biocides were analysed using two complementary methods: a group including glyphosate and AMPA was analysed by high-performance liquid chromatography (HPLC)-MS/MS, while a second group was quantified by gas chromatography-mass spectrometry (GC-MS) following liquid-liquid extraction. Total suspended solids (TSS) and water hardness were measured according to standard protocols.

Method performance, including limits of detection (LOD) and quantification (LOQ), recovery rates, and specific instrument parameters for all analyses, are detailed in the Supporting Information (Section SI1.2). The full list of analytes, their associated methods, and respective LOQs are available in the published dataset [51].

Analytical uncertainty

Triplicate samples from both rivers were analysed on five sampling dates. The absolute distances between the chemical analysis results of the triplicates were calculated, and the absolute uncertainty for each parameter was derived as their 75th percentile using a conservative approach. In this calculation, censored values (below the LOQ) were assumed to be half the LOQ. For parallel analyses in which both analytical results were lower than LOQ, an uncertainty equivalent to half the LOQ was assumed. Where the LOD value was also reported, censored values were set to (LOQ + LOD)/2, with half the difference between the LOQ and LOD chosen as the absolute deviation for values below the LOQ but above the LOD. For non-detectable substances, the uncertainty of the results was taken as half of the LOD. The resulting analytical uncertainties for all parameter that could be quantified at least one are reported in detail in Table SI3.

Data analysis

Cleaning and use of data from continuous measurements

While continuous monitoring generally played an important role in describing the catchment's physical conditions and dynamics during the sampling period, and in supporting the interpretation of the results, different parameters also served specific purposes. Throughout the sampling period, we regularly checked the data generated by the continuous, inline measurements in order to identify any potential anomalies, flagged them for exclusion from further analysis.

Water level was used on the one hand to regulate the frequency of FPC sampling, and on the other hand, to calculate loads of trace contaminants, which are presented in the results as flow-weighted concentration averages for better comparability (see detailed explanation in the next section). Clean datasets of radar sensor measurements exhibit 99 % completeness at both stations. Discharge was calculated using a rating curve derived from nearby hydrological stations, with a relative error of ± 40 % chosen to represent uncertainty, based on a conservative assessment.

Turbidity and conductivity were used to verify the representativeness of the survey. The values measured by the inline sensors were used as a benchmark against which to validate the concentrations of TSS and total dissolved solids (TDS) in the GS and composite samples (TPC and FPC). The first processing step involved aggregating the data into 5-minute intervals by calculating the mean of the measurements. Linear interpolation was then applied to fill in any gaps of one hour or less in the time series, while gaps of more than one hour were retained as missing values. The final continuous turbidity measurement dataset is 99 % complete at Nodbach and 91 % complete at Wulka. These measurements were converted to TSS concentrations by comparing the corresponding values in samples where both were available. At Nodbach, the TSS concentrations derived from turbidity measurements were consistent with laboratory analyses. At Wulka, however, we identified a systematic overestimation of TSS in the inline measurements, which were corrected using a factor of 0.48. For further analysis, the 75th percentile of the differences between the laboratory measurements and the corrected turbidity values was used to represent the absolute error. Conductivity measurements show 99 % completeness at Nodbach and 96 % at Wulka, with no systematic deviation from handheld measurements. TDS values were derived from conductivity at a ratio of 1 $\mu S\ cm^{-1} \equiv 1$ mg dry matter (DM) l^{-1}, with the 75th percentile of absolute differences representing the error. To objectively assess the performance of the sampling methods against reference data (e.g., inline measurements), the following quantitative criteria were defined based on the relative deviation from the reference value: Good Agreement: Relative Deviation (RD) < ±10 %; Slight Deviation: ±10 % ≥ RD < ±30 %; Strong Deviation: RD ≥ ±30 %. Furthermore, to describe the nature of the error, results were classified as underestimation (RD < 0) or overestimation (RD > 0).

Processing and evaluation of trace contaminant concentrations

To assess the suitability of monthly GS for estimating average and maximum concentrations, or annual loads, the GS results were compared with those of the composite samples. To illustrate the variability of possible results based on GS, two different approaches were used to evaluate the GS: The first approach used a Monte Carlo simulation, in which 12 of 27 samples were used to calculate the primary metrics (annual mean, 90th percentile, load) to represent the monthly sampling intervals required by the EU-WFD. The sample selection was performed as a semi-random draw, a pick of one sample each month out of two to three sub-monthly samples per month. This was repeated 2^{12} times to simulate the distribution of the monthly sampling intervals required by the EU-WFD. The second approach used all 27 GS and a calculation method, which applied a monthly calculation prior to the calculation of the annual metric, which is in accordance with the Guidance on surface water chemical monitoring under the EU-WFD [8].

For average annual concentrations, the TPC method is considered to most closely approximate real conditions, as it averages the content of trace contaminants in equal sample volumes taken regularly and at short intervals over time. The annual average concentrations from GS were as the annual arithmetic mean calculated by the above mentioned two different methods. The reference value was obtained by calculating the arithmetic mean of the 26 TPC samples. For the sake of completeness, the arithmetic mean concentration of the 24–26 FPC samples is also shown for comparison, to provide additional information on whether this method produces similar or significantly different results.

For the annual maximum concentrations, the assessment is conducted using the 90th percentile of the monitoring results, in accordance with the requirements of Austrian legislation concerning Environmental Quality Standards for the chemical status assessment of surface waters [40]. The annual maximum concentrations from GS were as the annual 90th percentile calculated by the above mentioned two different methods. The initial assumption was that the 90th percentile of the concentrations of the FPC samples would most closely approximate the real conditions under the sampling strategies employed. This assumption is based on the fact that elevated concentrations are often associated with peak discharges. This primarily occurs when diffuse and discharge-driven inputs are the most relevant. Due to the increased frequency of sampling with increasing river flow, the FPC method is better able to capture such conditions than TPC sampling. TPC samples would allow for better detection of maximum concentrations if concentration peaks in the water occur independently of discharge events. However, due to their composite nature, the FPC and TPC samples will attenuate signals from short-duration concentration peaks. This results in a lower-bound estimate of the true concentration peaks. Therefore, for the purposes of this study, the results of FPC are compared to those of TPC, and both are then benchmarked against GS to quantify the overall under- or overestimation.

To evaluate the results regarding annual loads, the flow-weighted mean annual concentrations were calculated. These are in a fixed relationship to the annual loads and provide better comparability. Flow-weighted mean annual concentrations were calculated by estimating the loads for different sampling periods or times (flow multiplied by concentration), extrapolating to the annual load and dividing the annual load by the annual flow. For flow-weighted annual concentrations, the results obtained via the FPC method are considered to most closely approximate real conditions and are therefore used as the reference values. This is because, when taking composite samples for load calculation, it is crucial to ensure that the concentration used as the basis for the calculation is proportional to the discharge. To illustrate the variability in the results from 12 GS per year, the calculation was performed as mentined above. For the sake of completeness, the results of flow-weighted concentration of the TPC samples are presented as well, to provide additional information on whether similar or significantly different estimates are obtained with this method.

To distinguish systematic from random differences in concentrations, the absolute analytical uncertainty was calculated by the gaussian law of error propagation (applied equations are given in Equations SI1–4) and is shown as an error bar in the figures. Where necessary, suitable methods were used to deal with censored data, essentially following the recommendations of Helsel [18]. The 'Regression on Order Statistics' (ROS) method was used to calculate statistical position descriptors such as the mean or 90th percentile. A log-normal distribution of the data was assumed for concentrations below the LOD or the LOQ.

To statistically quantify the deviation of the GS-based results from the reference values from TPC and FPC, respectively, we calculated the median deviation (MD) and the the probability of underestimation (PUE) for each site and contaminant (applied equations are given in Equations SI5 and 6).

Finally, for a series of trace contaminants for which the analytical results permitted quantitative evaluation, the potential for different assessments of compliance with environmental standards based on the results of the three different sampling techniques was evaluated. For this purpose, different environmental standards were considered (see full list in Table SI4): EU and national Environmental Quality Standards (EQS) currently valid [40], proposed new EU EQS [10] as well as quality criteria proposed by Junghans [21].

Software

All data analysis was conducted in R 4.4.2 [41] using mainly packages 'data.table' 1.17.0 [1], 'ggplot2' 3.5.1 [54], 'DTSg' 2.0.0 [19], 'ggsci' 3.2.0 [58], 'NADA' 1.6–1.1 [29], 'patchwork' 1.1.3 [35].

Results

Implementation rate of the sampling plan

The sampling plan was implemented with some adjustments due to technical and logistical challenges. As planned, 26 samples were collected at each site through a biweekly rhythm for TPC. For FPC, 26 samples were collected at the Nodbach, but only 24 were obtained at Wulka due to equipment failure during the high-flow events of April 2024. However, two additional GS enabled us to separately capture a flood event with a return period of over one year (>HQ1) in June 2024, with an additional GS collected at each station. This resulted in a total of 27 collected GS at each site. The Wulka sample was taken shortly after the main flow peak, while the Nodbach sample was collected during the declining flood wave, once the flow had already reached mean annual discharge (MQ) levels.

The sampling interval for FPC had to be regularly adjusted to achieve the minimum required sample volume for chemical analyses and to avoid overfilling of the storage bottles. However, the storage bottles had to be changed several times - up to three times within the 14-day sampling period - to enable continued sampling. This was particularly true of the Nodbach, given its highly dynamic and variable discharge pattern, with minimal flows in summer that increased significantly and quickly during storm events. The Wulka River was easier to handle in this respect, as the flow variability was smaller and the storage bottle volume was sufficient in most cases. Nevertheless, at both stations, it was only possible to sample the start of events exceeding HQ1, because the sampling interval increased so much that the storage bottles reached their maximum volume so quickly that it was not possible to react logistically in time to replace them. For TPC, changing the storage bottles was not necessary due to the fixed sampling interval. However, also in this case small deviations from the planned sampling duration could not always be avoided due to clogging of the sampling hose after sedimentation at the inlet. Additionally, some sub-samples could not be collected due to a frozen sampling hose in winter, or because the inlet was above the water surface due to a very low water level, which lasted up to one day.

Despite the technical and logistical challenges, the deviation from the planned sampling time was less than one day on average. A detailed summary of the final number of samples and their sampling duration is provided in Table SI5.

Sampling representativeness

Throughout the duration of the sampling period, the river discharge at both sites was broadly in line with the long-term average. Various periods of low and high flow were recorded, particularly extreme in September 2023 and June 2024, respectively. The temporal concentration profile of TDS shows the usual and expected pattern of dilution during runoff events. Exceptional peaks in TDS above 2000 mg DM l^{-1} in both rivers in December 2023 were most likely caused by inputs of de-icing road salt. The temporal concentration profile of TSS indicates that the high-flow events in spring 2024 caused very elevated concentrations of suspended matter above 1000 mg DM l^{-1}. Therefore, the one-year survey covered a wide range of heterogeneous hydrological conditions (detailed time series of river discharge, TDS and TSS, including the timing of sampling, are shown in Fig. SI1). This provides a solid basis for addressing the study's questions comprehensively, considering different and variable situations of emissions and transport processes.

The comparison between the annual average concentrations of the GS and composite samples for TDS and TSS and those of the inline continuous measurement data, used to evaluate the representativeness of the sampling methods, is shown in Fig. SI 2. For the annual mean concentrations, the TPC samples are expected to provide the most accurate values. This is confirmed at both sites by the good agreement between the mean TPC sample values and the reference values from the inline measurements for TDS and TSS. However, due to data gaps from turbidity sensors during extreme high flow events, the mean derived from them is considered to be a partial underestimate. Determining mean annual concentrations from FPC samples leads to a slight underestimation in the TDS and to a strong overestimation (RD = 151 %) in the TSS compared to the inline data. This is expected because flow-proportional sampling has a higher sampling frequency at higher flow rates and therefore tends to generate samples richer in TSS and poorer in TDS because of dilution. GS only provides results in good agreement with inline data for TDS, as in this case the influence of discharge events is comparatively small. Since, with one exception, GS were not taken specifically during high flow events, samples rich in TSS are underrepresented and the averaging leads to a slight underestimation (RD = – 14 to – 21 %) of the real conditions.

For the maximum annual concentrations, the FPC samples are expected to produce values that are most similar to those obtained from the inline measurements. This was not confirmed, as the TPC produced the most accurate results, showing good agreement (Fig. SI2). The FPC showed strong deviations for TSS (RD = 114 %) and good agreement for TDS at Wulka, with slight underestimation in Nodbach. The results obtained are analogous to those of the annual mean concentrations. It is crucial to recognise that the maximum annual concentrations are expressed as the 90th percentile. This outcome suggests that genuinely extreme concentration events occur less frequently than 10 % of the time in this catchments. Consequently, these rare extremes do not exert a substantial influence on the 90th percentile value, which is primarily determined by the less extreme concentrations. FPC sampling over-represents these rare events during compositing, leading to deviations, especially at Nodbach.

For the flow-weighted mean annual concentration, which is representative of load calculations, the FPC samples are expected to produce values that are most similar to those obtained from the inline measurements. This is confirmed for TDS in both rivers showing good agreement (Fig. SI2). For TSS, the flow-weighted mean concentrations determined using FPC samples also give values closest to the inline reference values in the Nodbach, demonstrating good agreement. These results confirm that flow-weighted concentrations of TDS can be satisfactorily determined with good agreement to slight deviations (SD = – 22 to 20 %) using either GS or TPC sampling. However, accurate estimation of TSS loads requires FPC sampling, as both GS and TPC sampling exhibit strong underestimations (SD = – 77 to – 88 %). However, for the Wulka this comparison could not be conducted due to incomplete inline measurement datasets.

In general, the representativeness of the sampling strategy for each specific purpose was confirmed. For further comparisons of the trace contaminant results, we therefore consider TPC sampling results to be the reference for annual mean and maximum values, while FPC sampling results are considered to be closer to the real values for flow-weighted annual mean concentrations or loads.

Detection frequency and temporal variability

Of the 450 trace contaminants analysed, a total of 96 were detected above the LOQ at least once. Figure 2 illustrates differences in detection frequency and measured concentration level both between sites and sampling techniques, using selected examples of each group of contaminants. Illustrations of the detection frequency for all trace contaminants that were detected above the LOQ at least once can be found in the Supplementary Information (Fig. SI3–5)

Among the eight PTEs, only silver (Ag) was never detected. Cadmium (Cd) was rarely detected and was found more frequently in the composite samples than in the GS (Fig. 2 and SI 3). The dissolved fraction of lead (Pb) has high proportion of censored values, whereas measurements for all the other PTE were above the LOQ in almost 100 % of samples taken using all three techniques. Whereas total concentrations exhibit pronounced temporal variability throughout the year, with higher values in spring and summer due to increased sediment transport during high flow events, only the dissolved fraction of arsenic (As) exhibits this behaviour, with considerably lower levels observed in winter. No significant differences were observed between the two sites, but there are clear differences in the temporal variability of concentration levels depicted by the different sampling techniques.

The results for the four pharmaceuticals differ significantly between the two sites (Fig. 2 and SI3). In the Wulka, carbamazepine and diclofenac were present in all samples, while ibuprofen and sulfamethoxazole were present in between 50 % and 100 % of samples. Concentration levels varied widely, with no discernible seasonal pattern. Furthermore, we could not identify any pronounced peak in the concentration of the Wulka due to point source discharges from WWTPs during periods

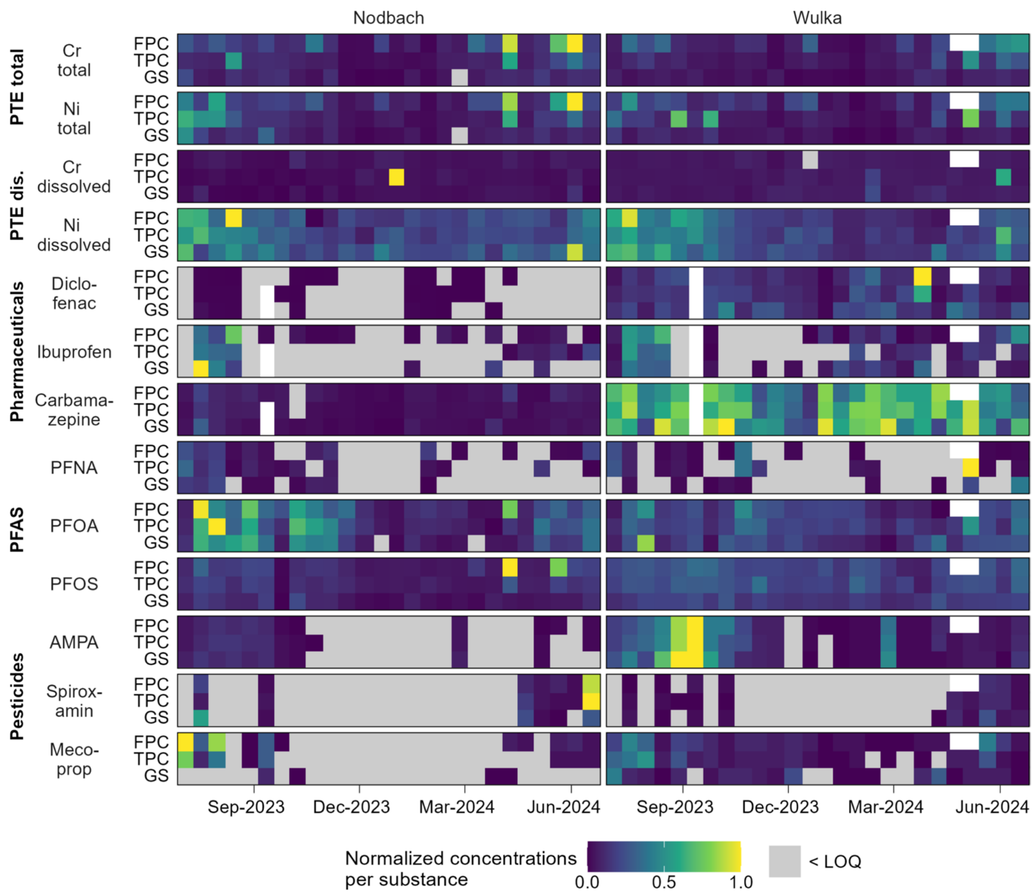

Fig. 2 Heat map of normalised concentration levels of selected compounds, which are examples of all the investigated groups of contaminants, measured in samples obtained using three different techniques at both sites. Grab samples (GS), time-proportional (TPC) and flow-proportional (FPC) composite samples

of low flow, as described in the literature [16, 57]. Surprisingly, carbamazepine was detected in over 90 % of the Nodbach samples, albeit at much lower concentrations, despite the absence of WWTP effluent discharge. Diclofenac and ibuprofen were also present at this site sometimes, with a higher detection frequency in composite samples (36–62 %) than in GS (23–31 %). In general, the detection of these pharmaceuticals, which are used exclusively in human medicine, in the Nodbach may be due to combined sewer overflows – as reported e.g. by Yang et al. [59] - or incorrect connections to the rainwater sewer system, but also to infiltration into groundwater through leaky sewer systems or disposal facilities. Interestingly, elevated ibuprofen values were observed in the Nodbach in summer, whereas the values were below or close to the LOQ for the rest of the year. While there was no correlation with precipitation events, there may be a connection with a cultural event that attracts many tourists to the sub-catchment during that period.

Of the 404 pesticides analysed, 58 were detected, with most being found in fewer than 20 % of the samples (Fig. 2 and SI4). The most frequently detected compounds were the herbicides glyphosate and AMPA, MCPA, mecoprop and terbutryne, as well as the insecticide gamma-hexachlorocyclohexane (lindane), with more frequent detection in the Wulka (~95 %) than in the Nodbach (11 %). A clear seasonal effect was visible in the Nodbach, with the highest frequency occurring between July and October, and no detections between December and March. This seasonal effect was less pronounced in the Wulka, where many pesticides were consistently detected until the end of October (e.g. tebuconazole, boscalid and spiroxamine), until December (MCPA, diuron, thiabendazole and imidacloprid), or throughout the entire year in the case of three pesticides and one metabolite (mecoprop, lindane, terbutryne and AMPA). However, a certain degree of seasonality in concentration levels was evident, with higher values generally being recorded during the growth period. It is important to note that some substances, such as thiabendazole and carbendazim and, even more pronouncedly, lindane, were either not detected at all or were detected only once in GS, yet were repeatedly or consistently measured above the LOQ in composite samples. The use of lindane as an insecticide in agriculture has been banned in the EU since 2007. Nevertheless, legacy emissions from its former use in wood treatment could still be a factor, as could its emissions from permitted use in human medicine as a second-line treatment for head lice and scabies. Comparing the two rivers yielded further unexpected findings. With the exception of herbicides with known urban applications such as diuron, terbutryne and mecropop, and the insecticide lindane used in human medicine to treat parasites, most investigated pesticides can be attributed to diffuse inputs from agriculture. However, the monitoring results show higher concentrations of all frequently detected substances in the Wulka than in the Nodbach, except for the fungicide spiroxamine. Additionally, the continuous presence of glyphosate and its metabolite AMPA throughout the year suggests relevant input via WWTP discharges. One possible explanation is that they originate from detergents that undergo in-situ transformation in WWTPs [12]. Current investigations have unearthed an unexpected and at present still inexplicable presence of glyphosate and AMPA across a wide range of Austrian municipal WWTPs [30], which lends weight to this assumption.

Regarding PFAS, 27 of the 34 compounds analysed were detected (Fig. 2 and SI5). These can be divided into three groups according to their frequency of detection. Five perfluoroalkyl carboxylic acids (PFCA) and three perfluoroalkyl sulfonic acids (PFSA), encompassing short-chain compounds, PFOA and PFOS, were detected in almost all samples. Two long-chain PFCA (PFNA and PFDA), the fluorotelomer 6:2 FTS as well as ADONA and GenX, substitute compounds of PFOA, were detected to varying degrees depending on the sampling technique and site. The remaining compounds were detected only sporadically. Among PFCA, short-chain compounds exhibit variable concentrations throughout the year, with no significant difference between the two sites. Conversely, PFSA concentrations are generally higher in the Wulka than in the Nodbach. ADONA and PFDS were mainly measured in both water bodies in autumn (between October and December), while PFNA and 6:2 FTS (in the Nodbach) were more frequently detected between July and December, and from May onwards. In spring, 8:2 FTS was occasionally measured at comparatively high concentrations in the Wulka. The GenX concentrations in the Nodbach in spring 2024 are notable. These were found in a GS in April and in four consecutive TPC samples. They were also found in FPC samples in May. The temporal variability (chemographs) of all trace contaminants analysed with at least one concentration above LOQ is provided in Figs. SI6–21.

Comparison of annual mean, flow-weighted mean and maximum concentrations

PTE – total content

PTEs are discharged into rivers via WWTPs and groundwater on a fairly continuous basis [32]. Additionally, short-term inputs driven by precipitation events through erosion, as well as via combined sewer overflows and separate sewer discharges, play a significant role [25, 34, 53]. The transport of PTEs in water bodies is largely influenced by river discharge, which controls the movement of suspended particles. With high log K_{oc} values ranging from 3.11 to 3.58 [15], PTEs tend to bind strongly to these particles, making their transport highly dependent on hydrological conditions.

The GS technique used in this study tends to poorly depict precipitation-driven short-term events of increased transport. Consequently, GS did not produce reliable estimates of average or maximum PTE concentrations, as illustrated in Fig. 3 for Cr and Ni. As reported in detail in Table SI 6 and illustrated in Fig. SI 22 for all PTEs, a considerable systematic underestimation of mean annual concentrations was found for almost all PTEs, with a factor mostly below 0.8 (the ratio of the concentration determined from GS as the median of the distribution of mean values of semi-randomly selected 12 samples, divided by the mean concentration of the reference values from TPC samples). Taking into account the random error due to sampling time, the probability of underestimating the reference values ranges from 63 % to 100 %. Given the importance of short-term events in the emissions and transport of PTEs in rivers, it is not surprising that maximum annual concentrations are underestimated via GS to an even more pronounced extent than average concentrations.

FPC also significantly overperformed compared to TPC when it came to estimating the maximum concentrations of As, Cu, Cr, Pb, Cd and Zn (the latter two in the Nodbach only), as it also overrepresents the PTE transport during the less frequently occurring high-flow and high-turbidity events. For all PTEs and at both sites, the flow-weighted mean concentration is largely underestimated by both GS and TPC methods. The results show that, on average, Pb loads estimated based on 12 GS samples correspond to only a factor of 0.1─0.2 of those estimated via FPC samples. For the other PTEs, the estimated range is approximately 0.2-─0.5 times of the reference values based on FPC samples. However, semi-random combinations of 12 GS that included the HQ1 sample led to a significant shift towards higher flow-weighted mean concentrations. This indicates that a stratified GS approach at different flow levels could partly offset the limitations of low-frequency GS for load calculation purposes.

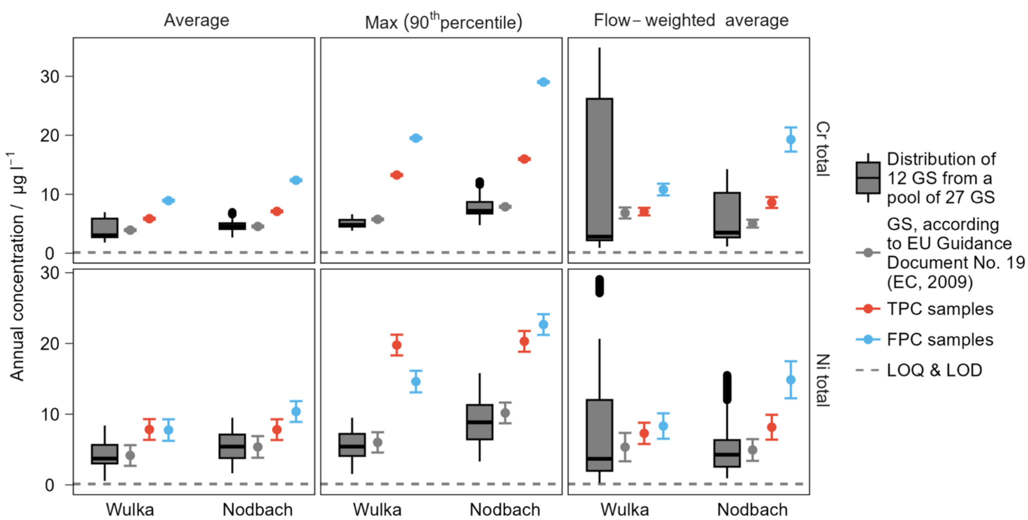

Fig. 3 Comparison of the annual total concentrations (incl. uncertainty) of selected PTE from the composite samples and from 12 monthly GS (as a distribution of 2^{12} combinations and according to EU Guidance Document No. 19 [8]). Left: annual mean concentrations; middle: annual maximum concentrations (90th percentile); right: flow-weighted annual mean concentrations. The annual concentrations from GS are shown at half their LOQ if they fall below the LOQ

PTE – dissolved fraction

A recent investigation of PTE dynamics during high-flow events in the same case study area identified significant differences in dissolved PTE concentrations during different events, which can be exploited to distinguish between event types [25]. However, it also showed that variability in concentration was much lower than that observed for total PTE content. The findings of our study confirm these observations.

As illustrated in Fig. 4 for Cr and Ni and detailed in Table SI6 and Fig. SI23 for all dissolved PTEs, determining annual averages from 12 GS performed significantly better than for total PTEs. In most cases, only minor systematic errors were found for both rivers. However, in the case of Cr and Cu, a highly probable underestimation of 15–20 % was found in the Wulka, and of up to 40 % in the Nodbach for Cr.

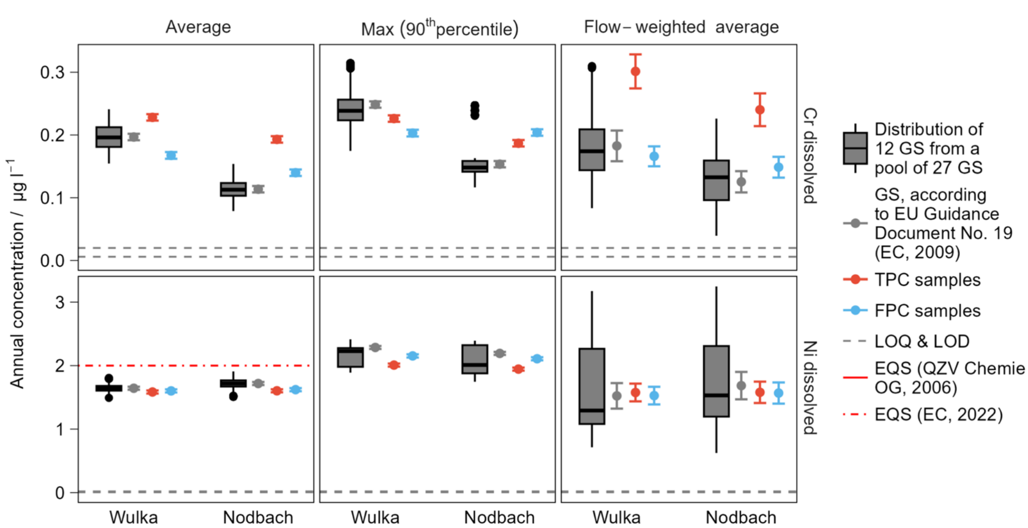

Fig. 4 Comparison of the annual dissolved concentrations (incl. uncertainty) of selected PTE from the composite samples and from 12 monthly GS (as a distribution of 2^{12} combinations and according to EU Guidance Document No. 19 [8]). Left: annual mean concentrations; middle: annual maximum concentrations (90th percentile); right: flow-weighted annual mean concentrations. The annual concentrations from GS are shown at half their LOQ if they fall below the LOQ. Limits not shown: Cr: 8.5 µg l^{-1} (AA-EQS; [40]), Ni: 4 µg l^{-1} (AA-EQS; [40])

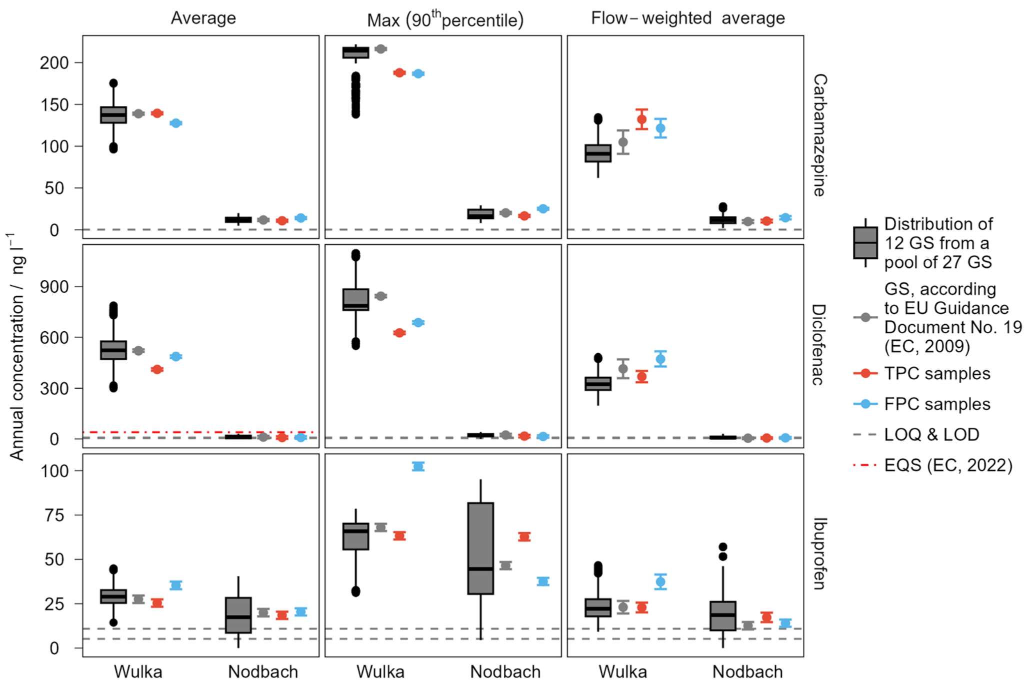

Fig. 5 Comparison of the annual concentrations (incl. uncertainty) of selected pharmaceuticals from the composite samples and from 12 monthly GS (as a distribution of 2^{12} combinations and according to the EU Guidance Document No. 19 [8]). Left: annual mean concentrations; middle: annual maximum concentrations (90th percentile); right: flow-weighted annual mean concentrations. The annual concentrations from GS are shown at half their LOQ if they fall below the LOQ. Limits not shown: carbamazepine: 2500 ng l^{-1} (AA-EQS; [10]), ibuprofen: 220 ng l^{-1} (AA-EQS; [10])

Regarding the determination of maximum annual concentrations, the monitoring approach based on 12 GS produced highly variable results ranging from lower to higher concentrations than the composite samples. The results also show that, although on average low-frequency GS are more suitable for determining annual loads of dissolved PTEs than total PTEs, significant deviations from the FPC-based reference load can occur depending on the timing of sampling. Such deviations resulted in overestimations of 30–40 % for Pb and underestimations of 35 % for Cu and Zn. These outcomes are consistent with those observed for TDS and corroborate the expectation that the dominant share of dissolved PTE input occurs through point discharges from WWTPs and through groundwater base discharge.

Compliance assessment with the EQS, which are currently valid for dissolved PTEs in Austria, indicates no exceedance and is consistent across the three different sampling techniques.

Pharmaceuticals

For widely used pharmaceuticals from human medicine, which are emitted primarily via municipal WWTPs without large temporal fluctuations, the results exhibit patterns comparable to those of TDS and dissolved PTEs (Fig. 5 and Fig. SI24). This is because they are transported in rivers in dissolved form, due to their poor sorption with log K_{oc} ranging between 1.86–3.40 [23, 42].

The medians of the annual average values from 12 GS tend to be close to the reference values from TPC samples, with a deviation factor close to one (Table SI6). However, there is a certain probability, although quite low, of underestimating the reference values in both rivers compared to other trace contaminants due to random error from variability in monthly samples.

For diclofenac in the Wulka, the mean concentration derived via TPC sampling is considerably lower than the median of the mean values from GS. This suggests that mean values from low-frequency GS likely lead to an overestimation of real values on average, as short-term phases involving the dilution of point-source inputs via WWTPs during increased river flow conditions are generally underrepresented in low-frequency sampling. Consequently, the maximum concentrations of carbamazepine, diclofenac and sulfamethoxazole in the Wulka tend to be higher with GS compared to the values obtained via TPC, due to the inherent averaging effect of composite samples which integrates periods of high dilution during increased flow.

Regarding flow-weighted mean values, the results obtained via GS show an underestimation by 20–30 % with very high probability in the Wulka, whereas the

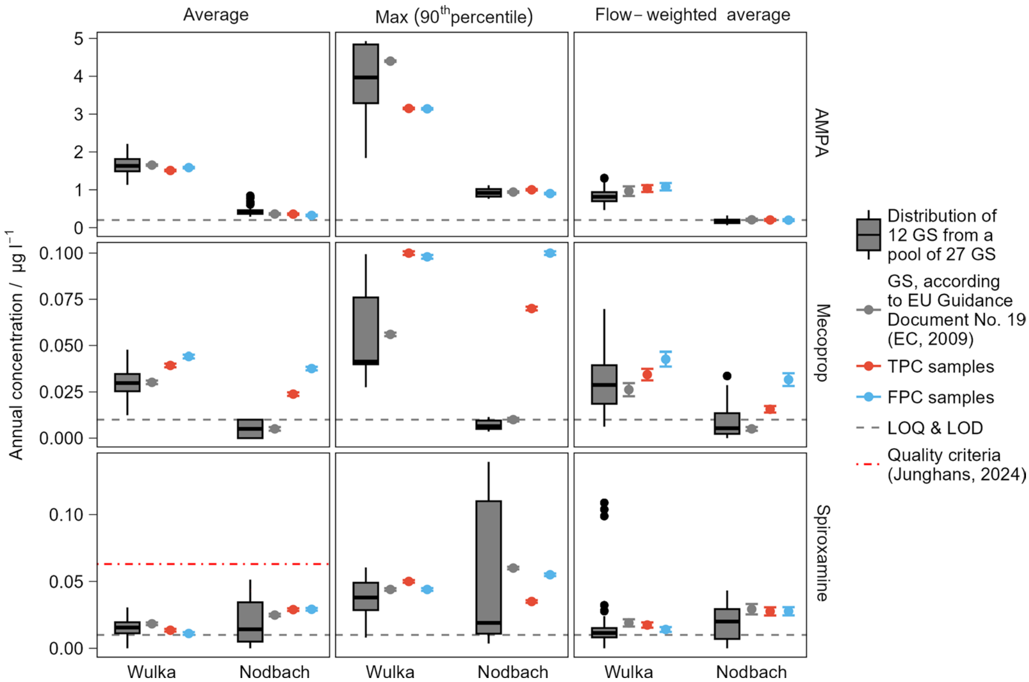

Fig. 6 Comparison of the annual concentrations (incl. uncertainty) of selected biocides and pesticides from the composite samples and from 12 monthly GS (as a distribution of 2^{12} combinations and according to EU Guidance Document No. 19 [8]). Left: annual mean concentrations; middle: annual maximum concentrations (90th percentile); right: flow-weighted annual mean concentrations. The annual concentrations from GS are shown at half their LOQ if they fall below the LOQ. Limits not shown: AMPA: 1500 µg l^{-1} (AA-EQS; [21]), mecoprop: 0.8 µg l^{-1} (AA-EQS; [21])

GS-based estimates correspond well with the reference values from FPC samples in the Nodbach, where both concentration levels and variability are much lower.

With respect to compliance with the currently valid or proposed environmental standards, the results obtained using all three sampling techniques are fully consistent, indicating clear exceedance of the proposed Annual Average EQS (AA-EQS) for diclofenac in the Wulka, and compliance with all other standards at both sites.

Biocides and pesticides

The heterogeneous temporal variability in the occurrence of the investigated pesticides and their concentration levels is reflected in the differing performance of GS in correctly estimating annual average concentrations (Fig. SI25–28).

In the Wulka in particular, we identified only slight deviations from the reference values obtained from TPC samples in terms of annual mean values for several substances, with a low probability of these values being underestimated (Table SI6). Figure 6 illustrates this for AMPA and spiroxamine in the Wulka, and the same applies to glyphosate, tebuconazole, terbutryne, boscalid and imidacloprid. These results suggest that a substantial proportion of the input is quite constant via groundwater (Wulka and Nodbach) and/or WWTPs (Wulka).

However, a potential overestimation of the annual mean values in the Wulka of approximately 30 %, based on GS, was found for other substances such as dimethenamid and diuron, though with a low probability. Conversely, estimates of annual average concentrations for other substances based on GS exhibit a highly probable and pronounced underestimation ranging from 55 % to 100 %. This likely reflects the effects of short-term pollution episodes, which GS poorly capture. Figure 6 exemplifies this pattern through the results of mecoprop at both sites and spiroxamine in the Nodbach. The same also applies to MCPA, metolachlor, benalaxyl and lindane.

Comparing the maximum concentrations estimates based on GS with the TPC samples shows clear discrepancies. For a number of substances such as mecoprop, and to a certain degree also spiroxamine, a monitoring concept based on 12 GS leads to considerable underestimation. Conversely, substances such as AMPA, cyprodinil and ethofumesate were recorded in the Wulka at higher concentrations in GS than in composite samples. Finally, similar maximum concentrations were determined for substances such as tebuconazole via the different sampling techniques.

Load calculations also require differentiation between substances. Flow-weighted averages for glyphosate, tebuconazole and imidacloprid in the Wulka, and for boscalid in the Nodbach, show almost no deviation between GS- and FPC-based estimates. However, for most other substances, GS-based estimates lead to varying degrees of underestimation. The average underestimation ranges from 25 % for AMPA in the Wulka to 50 % for spiroxamine and terbutryne in the Nodbach, with extreme cases reaching 90 % underestimation for mecoprop in the Nodbach and a complete failure to detect lindane in both rivers.

With regard to compliance assessment with environmental standards, this could be evaluated against the proposed EQS for glyphosate and nicosulfuron [10], and for the currently valid EQS for lindane [40]. The results show that the assessment based on the three different sampling techniques for nicosulfuron is highly consistent, indicating compliance with the maximum allowable concentration EQS (MAC-EQS) but exceedance of the AA-EQS at both sites.

The glyphosate assessment is also largely consistent, indicating compliance with the AA-EQS and MAC-EQS at both sites. However the assessment shows an exceedance of the stricter AA-EQS for the protection of surface waters used for drinking water extraction at both sites. The exception is the failure of TPC sample-based assessment to identify exceedance of the AA-EQS in the Nodbach. As previously mentioned, lindane represents an extreme case of discrepancies in detection frequency in the Wulka. This is reflected in the compliance assessment, in that exceedance of both the AA-EQS and the MAC-EQS in this river is only identified via composite samples.

PFAS

PFAS can enter surface water bodies via a variety of emission pathways. These include diffuse inputs via contaminated groundwater, surface runoff, urban stormwater drains and combined sewer overflows, as well as point discharges from industrial and municipal wastewater treatment plants. The contribution of each of these routes to the overall input into rivers varies extensively depending on the specific PFAS compounds and the catchment characteristics [24, 31].

From a physicochemical perspective, the PFAS investigated exhibit a wide range of sorption potentials, with log K_{oc} values ranging from 1.54 to 3.60 [46]. range reflects the established relationship that short-chain PFAS have lower log K_{oc} values and a higher water solubility, while longer-chain compounds are more prone to sorption.

The comparison of the effectiveness of different sampling techniques in determining the annual average concentration of PFAS in the Wulka and Nodbach rivers exhibits a heterogeneous picture. This is exemplified in Fig. 7 for PFOS, PFOA and PFNA, with a full overview provided in the SI (Fig. SI29–31).

For most PFAS compounds, the annual average concentration determined via GS deviates from the reference value obtained via TPC sampling. PFPeA is the only compound for which the annual average concentration determined via GS does not deviate from the reference value at both sites. This is true for PFOA and PFPeS only in the Wulka, and for PFHxA and PFBS only in the Nodbach. For these compounds in one of the rivers, and for PFHpA, PFNA, PFHxS, PFOS, 6:2 FTS, and the sum parameter PFOA-equivalent ($\Sigma PFAS_{24}$) in both rivers, highly probable underestimations of between 10 % and 40 % were identified (Table SI6). This suggests that both systematic and random errors can lead to significant underestimation of mean annual concentrations in a monitoring concept based on 12 samples.

Regarding maximum annual concentrations, the vast majority of PFAS tend to be underestimated via GS compared to TPC samples. Annual loads tend also to be underestimated via GS compared to FPC samples for the vast majority of PFAS. The extent of underestimation ranges from 10–20 % for short-chain PFCAs and PFSAs, and PFOA in the Wulka, to high degrees of around 70 % for PFOS and 6:2 FTS in the Nodbach.

The case of PFNA, which has a toxicity relative potency factor (RPF) of 10 compared to PFOA, deserves special attention [5]. Similar to the pharmaceutical ibuprofen, the measured concentrations of this compound were often close to the LOQ and highly variable over time. As observed for ibuprofen, while composite samples clearly demonstrate its presence, this compound can likely go undetected above the LOQ in 12 GS. Due to its high RPF, such differences have significant implications for potential compliance assessments regarding the proposed $\Sigma PFAS_{24}$.

In terms of compliance assessment with environmental standards, all three sampling methods produce the same results. They all indicate that the currently valid AA-EQS for PFOS is exceeded in both Wulka and Nodbach, as well as the specific thresholds derived from the proposed AA-EQS for PFOA-equivalents based on the RPF of PFOS and PFNA in Wulka and Nodbach, respectively.

Discussion

The results of the study largely confirm expectations based on our current knowledge of emission patterns and river transport dynamics, as well as our understanding of the role of temporal variability and contaminant sorption behavior in the performance of different monitoring approaches for different groups of trace contaminants.

However, the study also yielded some unexpected findings and raised new questions.

The poor performance of low-frequency GS in depicting chronic exposure, and even more acute exposure and transported loads, of total PTEs confirms what has already been widely documented not only for PTEs, but also for TSS and other substances with dominant particulate-bound transport, such as for instance phosphorus and polycyclic aromatic hydrocarbons (PAHs) [11, 38, 39, 47]. In light of the substantial existing scientific knowledge in this area, including total PTEs in the study was not intended to generate new insights into them per se, but rather to validate the survey's methodologies and results, and to cover a broad spectrum of emission sources, pathways, and environmental fates, enabling more insightful comparisons between groups of contaminants. Furthermore, for contaminants mainly transported attached to soil and sediment particles, due to their high log K_{oc} values (> 3.3), increasing the sampling frequency may be insufficient to obtain accurate estimates of river concentrations and loads. As Zoboli et al. [61] demonstrated for PAHs, monitoring approaches that rely exclusively on bulk water samples can lead to severe underestimations, and complementary sampling and analysis of suspended particulate matter are needed to ensure robust assessments.

The main findings on human pharmaceuticals and dissolved PTEs are consistent with the conclusions derived by Götz et al. [17] from a simple, exposure-based, theoretical methodology. This agreement is logical, as both contaminant groups are transported in the dissolved phase. For PTEs, a small dissolved fraction persists, while pharmaceuticals are known to exhibit poor sorption regardless of their theoretical log K_{oc} values [42]. Götz et al. [17] suggested that for highly persistent contaminants that are continuously released into surface waters, GS-monitoring may be sufficient; however, they recommended the use of TPC samples. Similarly, Petrie et al. [36] proposed that low-frequency GS can provide an adequate initial overview of pharmaceutical emissions and pollution levels; however, this should be viewed primarily as a screening approach to prioritise the allocation of monitoring resources, with integrated composite samples required for more advanced investigations and robust assessments.

Götz et al. [17] also reached similar conclusions regarding PFOS and PFOA, which were assumed to be emitted primarily via WWTPs at that time. However, recent years have seen a growing body of knowledge on these

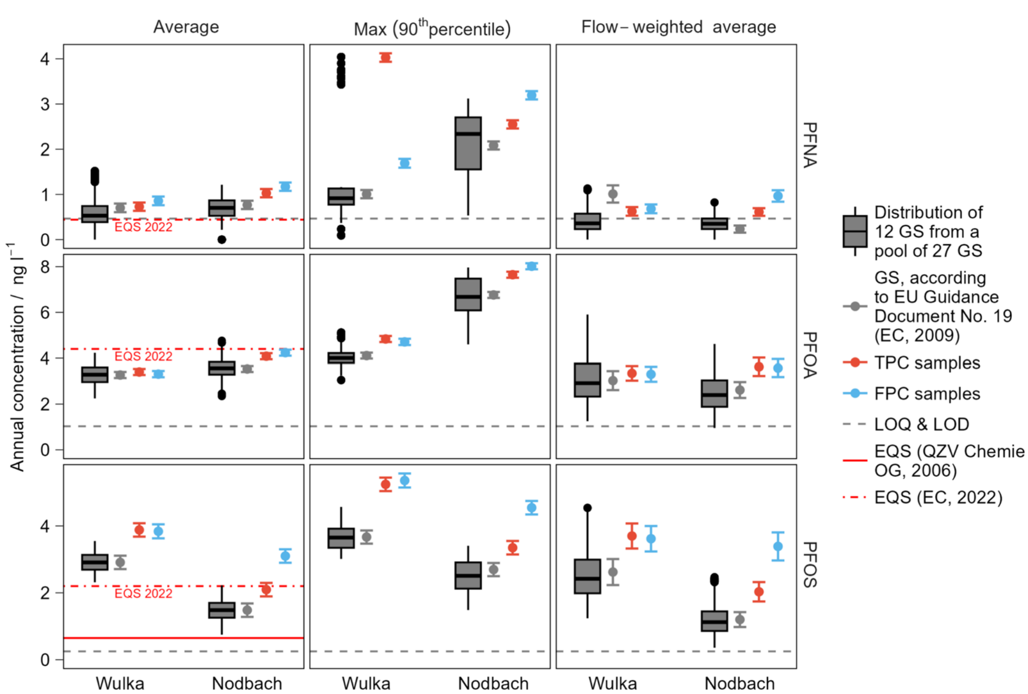

Fig. 7 Comparison of the annual concentrations (incl. uncertainty) of selected PFAS from the composite samples and from 12 monthly GS (as a distribution of 2^{12} combinations and according to EU Guidance Document No. 19 [8]). Left: annual mean concentrations; middle: annual maximum concentrations (90th percentile); right: flow-weighted annual mean concentrations. The annual concentrations from GS are shown at half their LOQ if they fall below the LOQ. The 'EQS 2022' proposal limits correspond to the proposed EQS for the sum parameter PFOA-equivalent multiplied by the specific RPF for each PFAS compound [10]

two compounds and a broader scope of PFAS, making it evident that adequately monitoring them in the environment is significantly more complex. While WWTP effluents can play a dominant role in specific river catchments, these compounds enter surface waters via several routes, with multiple diffuse emission pathways being particularly significant [24, 28, 31, 60]. This complexity is further compounded by the physicochemical diversity of PFAS themselves. The compounds investigated here exhibit a wide log K_{oc} range, meaning that their behavior in the river is not uniform; some remain dissolved, while others associate with particles. In our study, the important role that emissions via municipal WWTPs play is confirmed by generally higher concentration levels in the Wulka than in the Nodbach. Nevertheless, comparing the results obtained using different sampling techniques clearly shows that monitoring based on monthly GS carries a concrete risk of underestimating actual chronic and acute exposure levels, as well as transported loads, for several PFAS compounds. Fluctuations in concentrations and deviations in results were only poorly correlated with river discharge, suggesting that other emission dynamics are important factors.

The fact that correctly measuring pesticide and biocide concentrations in surface water presents a particular challenge in terms of sampling frequency has been amply shown in previous studies [6, 44, 52]. Our investigations have also largely confirmed this, with a number of substances (e.g. boscalid, MCPA and metolachlor) exhibiting pronounced seasonal occurrence and event-driven, fluctuating concentration levels. Pesticides cover a vast physicochemical diversity as a chemical class, with log K_{oc} values spanning a wide range from as low as 0.42 to as high as 5.31 [26], which indicates that some pesticides are highly mobile and dissolved while others are strongly particle-bound. This diversity helps to explain the observed variability in their environmental behavior. However, our survey also demonstrated that, contrary to our expectations based on current knowledge of their application and use patterns, other pesticides and biocides (e.g. glyphosate and AMPA) were detected months after the end of the growth period and even throughout the year. In some cases, even through monthly GS, only small deviations from the reference values for average annual concentrations were achieved. On the one hand, these findings support the conclusions regarding the persistence of certain groups of pesticides revealed by Herrmann et al. [20], who questioned the suitability of limiting the pesticide monitoring to the growth period. On the other hand, they highlight the need to identify unknown emission sources and routes for pesticides such as glyphosate and AMPA, which appear to be emitted fairly continuously from urban areas via municipal wastewater treatment plants. A potential source for these substances is detergent precursors that are transformed during treatment in WWTPs [12]. An additional, and not mutually exclusive, hypothesis relates to seasonal hydrological processes: the release of soil-bound glyphosate and AMPA during winter freeze-thaw events could also contribute to their sustained presence in waterways throughout the non-growing season [45]. It is worth noting that a higher level of contamination, in terms of both concentrations and detection frequency, was found for multiple pesticides in the Wulka than in the Nodbach, despite the fact that agriculture is very similar in both catchments.

In addition to the above points, a particularly noteworthy finding of our study is that multiple compounds, best represented by ibuprofen, lindane and PFNA, were present in the investigated rivers at demonstrable and non-negligible levels, and that however, they would certainly or very probably not have been detected via monthly GS. This suggests a widespread risk of underestimating the occurrence and level of pollution caused by contaminants with generally low but highly variable concentrations in rivers.

Besides confirming, expanding or questioning the expectations based on available knowledge of emission patterns and transport dynamics, the study's systematic comparison of different sampling techniques, quantification of deviation in statistical estimates, and quantification of underestimation probability is a significant contribution. This is particularly pertinent and relevant given that the monthly GS approach remains widely used for environmental quality standards compliance assessment, river load calculation and data basis for calibrating and validating models, despite growing awareness of these issues in the field of water quality management.

In our case study, despite the fact that GS led to considerable underestimations and sometimes also overestimations of the reference values, they led to consistent compliance assessments with environmental standards. The reason is to be found in the high degree of compliance or exceedance; in other words, the measured concentration levels are being far below or above the respective thresholds. If the concentration levels in rivers were to be closer to the standards, the sampling technique would indeed affect the assessment. This underscores the practical importance of selecting a monitoring method that is fit for purpose. We therefore present a summary of the suitability of the sampling methods depending on the assessment to guide best practice (Table 1). The 'conditional' rating indicates that the readers should refer to the detailed results to thoroughly evaluate the method's suitability based on specific circumstances and selected contaminants.

A number of limitations of the study must be acknowledged and considered. The definition of maximum concentrations varies between EU member states. For instance, Germany uses the 100th percentile [3], whereas this study adopts the Austrian 90th percentile [40]. If different percentiles were applied, the study's findings on maximum concentrations may differ significantly, potentially affecting compliance assessments or risk evaluations. Additionally, to evaluate the performance of GS in determining maximum annual concentrations, we compared the results obtained using GS with those obtained using TPC samples collected over two-week periods. This fulfilled the purpose of our research question, which was to assess the relative performance of GS rather than to estimate the most accurate values. However, accurately determining maximum concentrations would require either TPC sampling over much shorter time periods or high-frequency GS, both of which would incur much higher implementation costs. The two-week integration period for composite samples also means that a proportion of the sub-samples is stored for several days before analysis. We cannot exclude the possibility of degradation, transformation or other types of loss of our targeted analytes during this time. However, we minimised this risk by ensuring that the autosamplers were equipped to store the samples under refrigerated and dark conditions, as this has been shown to be the most effective storage method [37]. Furthermore, in the vast majority of cases, the deviation identified based on GS corresponded to an underestimation of the values obtained via composite samples. Therefore, considering potential losses in the composite samples would mostly serve to strengthen the conclusions drawn in the study.

For various reasons, high-frequency or time-integrated monitoring can be particularly important in headwater streams and, more generally, in small rivers. Agricultural headwaters are typically subject to disproportionate pressure from emissions of nutrients and pesticides, which negatively impact their chemical and ecological status and have cascading effects on the downstream river network [4, 52]. If WWTPs discharge into them, the low dilution of effluents can also lead to a disproportionate impact on water quality [22]. At the same time, these streams typically exhibit the greatest variation in streamflow and water quality [4], rendering low-frequency GS inadequate. The results of our study in the Nodbach support these observations in terms of: (i) highly variable contaminant concentrations, (ii) a higher extent of detection than expected based on knowledge of land use and wastewater infrastructure, and (iii) the concrete risk of overlooking or underestimating the occurrence of contaminants through monthly GS. At the same time, our survey showed that, particularly in the case of the Nodbach due to its low and highly variable streamflow, ensuring the continuity and regularity of FPC sampling was challenging and required considerable effort and resources. Therefore, while this may result in some underperformance, particularly with regard to load calculations, we propose the alternative implementation of TPC sampling or of flow-stratified GS depending on the available resources and the specific logistical conditions of each monitoring programme. In this context, passive sampling represents another promising alternative for capturing time proportional averages, often noted for its simpler implementation in remote or logistically challenging locations. However, it is a promising method for capturing time-proportional average concentrations. The validation of its application is an active area of research, particularly for reliable load calculation and for the diverse suite of trace contaminants studied here. It is not suitable for detecting maximum concentrations or loads.

Conclusions

This study systematically evaluated the performance of low-frequency grab sampling in accurately estimating annual average and maximum concentrations, as well as annual loads, of various groups of trace contaminants in rivers. For trace contaminants introduced predominantly continuously into surface waters, such as widely used pharmaceuticals or dissolved PTEs, approximate annual average concentrations can be estimated using monthly grab samples with no severe systematic bias. However, as random errors can lead to underestimation or overestimation, time-proportional or flow-proportional composite samples are more reliable if accurate estimates are required. Composite samples are particularly advantageous and are required for accurate estimates when emissions and riverine concentrations exhibit considerable temporal variability. Substances released seasonally, such as many agricultural pesticides, cause periods of pollution in watercourses that require specific attention through targeted composite sampling over longer periods of time. Contaminants introduced into watercourses during specific and short-term events, such as some pesticides and biocides, some PFAS and PTEs in their total content, cannot be adequately detected by low-frequency sampling. This applies to average annual concentrations but even more so to maximum concentrations and riverine loads. Using integrated composite samples, especially flow-proportional, performs significantly better for such contaminants. Alternatively, flow-stratified targeted grab samples can partially compensate for the limitations of low-frequency sampling. If contaminants are emitted in pulses of short duration, they may not be detected at all through grab samples. In such cases, integrated

Table 1 Suitability of the sampling methods for different contaminant groups depending on the objective of the assessment and on the presence or absence of relevant WWTP effluent discharges in the river catchment

Group	WWTP effluent	Annual mean			Max (90th percentile)			Annual riverine load		
		GS	TPC	FPC	GS	TPC	FPC	GS	TPC	FPC
PTE total	Yes	–	+	+/–	–	o	+	–	o	+
	No	–	+	–	–	o	+	–	–	+
PTE dissolved	Yes	+	+	+	+	+	+	+	+	+
	No	+	+	+	+	+	+	+	+	+
Pharmaceuticals	Yes	+	+	+	o	+	+	o	o	+
	No	+	+	+	+	+	+	+	+	+
Pesticides	Yes	+/–	+	o	+/–	+	+	+/–	+/–	+
	No	+/–	+	o	+/–	+	+	+/–	+/–	+
PFAS	Yes	–	+	o	–	+	+	–	+	+
	No	–	+	–	–	+	+	–	+	+

The suitability ratings are categorized as follows: Recommended (+), acceptable (o), conditional (+/–) and unsuitable (–)

composite samples, either time- or flow-proportional, are indispensable to ensure detection.

In our case study area, although the average and maximum concentrations estimated using different sampling techniques varied significantly, they led to a consistent assessment of compliance with the environmental standards either currently valid or proposed under the ongoing regulatory revision in the EU. This is because the measured concentrations were clearly above or below the thresholds set out in the environmental standards. However, in cases where the concentration level is closer to these thresholds, deviations identified based on different sampling techniques do indeed carry a considerable risk of leading to an incorrect assessment.

The study makes an important scientific contribution by quantifying deviations in statistical estimates and the probability of underestimation for various groups of contaminants and different types of rivers. This is important because the monthly grab sampling approach is still widely used for compliance assessment and different river basin management-related tasks, despite growing awareness among water quality experts of the issues presented in this work.

Abbreviations

$\Sigma PFAS_{24}$	Sum parameter of 24 specific PFAS expressed as a PFOA-equivalent concentration
6:2 FTS	6:2 Fluorotelomer sulfonic acid
8:2 FTS	8:2 Fluorotelomer sulfonic acid
AA-EQS	Annual Average Environmental Quality Standard
ADONA	4,8-Dioxa-3 H-perfluorononanoic acid
AMPA	Aminomethylphosphonic acid
DM	Dry matter
EC	Electrical conductivity
EPDM	Ethylene propylene diene monomer rubber
EPDM	Ethylene propylene dienemonomer rubber
EQS	Environmental Quality Standard
EU	European Union
FPC	Flow-proportional composite
GenX	Perfluoro-2-methyl-3-oxahexanoic acid
GS	Grab sampling/samples
GC	Gas chromatography
HPLC	High-performance liquid chromatography
HQ1	Flood event with a return period of one year
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
K_{oc}	Organic carbon partition coefficient
LC-MS	Liquid chromatography mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MAC-EQS	Maximum Allowable Concentration EQS
MCPA	2-Methyl-4-chlorophenoxyacetic acid
MQ	Mean annual discharge
PAHs	Polycyclic aromatic hydrocarbons
PE	Polyethylene
PFAS	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutanesulfonic acid
PFCA	Perfluoroalkyl carboxylic acids
PFDA	Perfluorodecanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPeA	Perfluoropentanoic acid
PFPeS	Perfluoropentanesulfonic acid
PFSA	Perfluoroalkyl sulfonic acids
PTE	Potentially toxic element
ROS	Regression on Order Statistics
RPF	Relative Potency Factor
SPE	Solid Phase Extraction
TDS	Total dissolved solids
TPC	Time-proportional composite
TSS	Total suspended solids
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

Supplementary Information

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Supplementary material 1

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Author contributions

N.W.: Formal analysis, Investigation, Data curation, Validation, Visualisation, Writing – Original Draft, Writing – Review and Editing; J.L.: Formal analysis, Investigation, Data curation, Validation, Visualisation; E.S.: Investigation, Data curation, Validation; C.H.: Formal analysis, Investigation; S.K.: Writing – Review and Editing, Validation, Investigation, Methodology, Data curation; K.K.: Investigation, Data curation, Validation; R.M.S.: Investigation, Data curation, Validation; J.K.: Resources, Writing – Review and Editing; M.Z.: Conceptualisation, Methodology, Supervision, Funding acquisition, Writing – Review and Editing; O.Z.: Conceptualisation, Methodology, Supervision, Project administration, Funding acquisition, Writing – Original Draft, Writing - Review and Editing;

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Data availability

The datasets generated and analysed during the current study are available in the TU Wien Research Data Repository under https://doi.org/10.48436/rms5d-yf550 (concentration data) or from the corresponding author on reasonable request (high-frequency data).

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Competing interests

The authors declare no Conflict of interest.

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References

1. Barrett T, Dowle M, Srinivasan A et al (2024) data.table: Extension of 'data.frame'. https://doi.org/10.32614/CRAN.package.data.table
2. Benisch J, Helm B, Chang X et al (2024) Can short-term online-monitoring improve the current WFD water quality assessment regime? Systematic resampling of high-resolution data from four Saxon catchments. Water 16(6):889. https://doi.org/10.3390/w16060889
3. BGBl. I S. 1373 (2016) Oberflächengewässerverordnung vom 20. Juni 2016 (BGBl. I S. 1373), die zuletzt durch Artikel 2 Absatz 4 des Gesetzes vom 9. Dezember 2020 (BGBl. I S. 2873) geändert worden ist. https://www.gesetze-im-internet.de/ogewv_2016/BJNR137310016.html
4. Bieroza M, Hallberg L, Livsey J et al (2024) Recognizing agricultural headwaters as critical ecosystems. Environ Sci Technol 58(11):4852–4858. https://doi.org/10.1021/acs.est.3c10165
5. Bil W, Zeilmaker M, Fragki S et al (2021) Risk assessment of per- and polyfluoroalkyl substance mixtures: a relative potency factor approach. Environ Toxicol Chem 40(3):859–870. https://doi.org/10.1002/etc.4835
6. Chow R, Scheidegger R, Doppler T et al (2020) A review of long-term pesticide monitoring studies to assess surface water quality trends. Water Research X 9:100064. https://doi.org/10.1016/j.wroa.2020.100064
7. Doppler T, Dietzel A, Wittmer I, et al (2020) Mikroverunreinigungen im Gewässermonitoring; Ausbau von NAWA Trend und erste Resultate 2018. Aqua &Gas 7/8 https://www.bafu.admin.ch/bafu/de/home/themen/wasser/fluesse-und-baeche/nationale-beobachtung-oberflaechengewaesserqualitaet--nawa-.html
8. EC (2009) Guidance on surface water chemical monitoring under the water framework directive. Guidance document No 19. https://doi.org/10.2779/72701
9. EC (2013) 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 Text with EEA relevance. http://data.europa.eu/eli/dir/2013/39/oj/eng
10. EC (2022) 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. https://environment.ec.europa.eu/publications/proposal-amending-water-directives_en
11. Elwan A, Singh R, Patterson M et al (2018) Influence of sampling frequency and load calculation methods on quantification of annual river nutrient and suspended solids loads. Environ Monit Assess 190(2):78. https://doi.org/10.1007/s10661-017-6444-y
12. Engelbart L, Bieger S, Thompson K et al (2025) In-situ formation of glyphosate and AMPA in activated sludge from phosphonates used as antiscalants and bleach stabilizers in households and industry. Water Res 280:123464. https://doi.org/10.1016/j.watres.2025.123464
13. EPA (2024) Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. https://www.epa.gov/system/files/documents/2024-01/method-1633-final-for-web-posting.pdf
14. European Environment Agency (2024) Europe's state of water 2024: the need for improved water resilience. Tech. rep., https://www.eea.europa.eu/en/analysis/publications/europes-state-of-water-2024
15. Fahimah N, Oginawati K, Suharyanto (2020) Fate and spatial distribution of Pb, Cd, Cu and Zn in the water column and in the surface sediment of indonesian estuary (Citarum River Estuary). E3S Web Conferences 148:07007. https://doi.org/10.1051/e3sconf/202014807007
16. Götz C, Bergmann S, Ort C et al (2012) Mikroschadstoffe aus kommunalem Abwasser - Stoffflussmodellierung, Situationsanalyse und Reduktionspotenziale für Nordrhein-Westfalen. Tech. rep., Ministerium für Klimaschutz, Umwelt, Landwirtschaft, Natur- und Verbraucherschutz NRW (MKULNV), https://www.lanuv.nrw.de/fileadmin/forschung/wasser/klaeranlage_abwasser/Abschlussbericht%20Mikroschadstoffe_komprimiert.pdf
17. Götz CW, Stamm C, Fenner K et al (2010) Targeting aquatic microcontaminants for monitoring: exposure categorization and application to the Swiss situation. Environ Sci Pollut Res 17(2):341–354. https://doi.org/10.1007/s11356-009-0167-8
18. Helsel DR (2012) Statistics for censored environmental data using Minitab®and R. John Wiley & Sons Inc Hoboken NJ USA. https://doi.org/10.1002/9781118162729
19. Hepp G (2023) DTSg: A Class for Working with Time Series Data Based on 'data.table' and 'R6' with Largely Optional Reference Semantics. https://cran.r-project.org/web/packages/DTSg/index.html
20. Herrmann LZ, Bub S, Wolfram J et al (2023) Large monitoring datasets reveal high probabilities for intermittent occurrences of pesticides in European running waters. Environ Sci Eur 35(1):90. https://doi.org/10.1186/s12302-023-00795-4
21. Junghans M (2024) Vorschläge des Oekotoxzentrums für Qualitätskriterien für Oberflächengewässer. https://www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/qualitaetskriterienvorschlaege-oekotoxzentrum
22. Kardos MK, Patziger M, Jolánkai Z et al (2025) The new urban wastewater treatment directive from the perspective of the receiving rivers' quality. Environ Sci Eur 37(1):10. https://doi.org/10.1186/s12302-024-01040-2
23. Kim S, Chen J, Cheng T et al (2025) PubChem 2025 update. Nucleic Acids Res 53(D1):D1516–D1525. https://doi.org/10.1093/nar/gkae1059

24. Kittlaus S, Clara M, van Gils J et al (2022) Coupling a pathway-oriented approach with tailor-made monitoring as key to well-performing regionalized modelling of PFAS emissions and river concentrations. Sci Total Environ 849:157764. https://doi.org/10.1016/j.scitotenv.2022.157764
25. Kittlaus S, Ščančar RM, Kozlica K et al (2025) Dynamics of potentially toxic elements in small rivers during high-flow events. J Contam Hydrol. https://doi.org/10.1016/j.jconhyd.2025.104659
26. Kobayashi Y, Uchida T, Yoshida K (2020) Prediction of soil adsorption coefficient in pesticides using physicochemical properties and molecular descriptors by machine learning models. Environ Toxicol Chem 39(7):1451–1459. https://doi.org/10.1002/etc.4724
27. Kromidas S (2011) Validierung in der Analytik, 2nd edn. Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim
28. Kurwadkar S, Dane J, Kanel SR et al (2022) Per- and polyfluoroalkyl substances in water and wastewater: a critical review of their global occurrence and distribution. Sci Total Environ 809:151003. https://doi.org/10.1016/j.scitotenv.2021.151003
29. Lee L (2020) NADA: nondetects and data analysis for environmental data. https://CRAN.R-project.org/package=NADA
30. Lenz K, Hartmann C, Narendja F et al (2024) Emissionen ausgewählter Stoffe aus kommunalen Kläranlagen. Tech. rep., Bundesministerium für Land- und Forstwirtschaft, Regionen und Wasserwirtschaft, Wien, https://www.bmluk.gv.at/service/publikationen/wasser/emissionen-ausgewaehlter-stoffe-aus-kommunalen-klaeranlagen.html
31. Liu M, Saracevic E, Oudega TJ et al (2025) Investigating the extent of PFAS contamination in the upper Danube basin across environmental compartments. Environ Sci Eur 37(1):99. https://doi.org/10.1186/s12302-025-01141-6
32. Madikizela LM, Chimuka L, Ncube S (2023) Metal pollution source apportionment in two important rivers of eastern cape province, South Africa: a case study of bizana and mthatha rivers. Environ Forensic 24(1–2):71–84. https://doi.org/10.1080/15275922.2021.1940382
33. Milačič R, Marković K, Marković S et al (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(12):4173–4186. https://doi.org/10.1007/s11368-023-03625-5
34. Nickel JP, Fuchs S (2019) Micropollutant emissions from combined sewer overflows. Water Sci Technol 80(11):2179–2190. https://doi.org/10.2166/wst.2020.035
35. Pedersen TL (2024) Patchwork: the composer of plots. https://doi.org/10.32614/CRAN.package.patchwork
36. Petrie B, Barden R, Kasprzyk-Hordern B (2015) A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res 72:3–27. https://doi.org/10.1016/j.watres.2014.08.053
37. Petrie B, Proctor K, Youdan J et al (2017) Critical evaluation of monitoring strategy for the multi-residue determination of 90 chiral and achiral micropollutants in effluent wastewater. Sci Total Environ 579:569–578. https://doi.org/10.1016/j.scitotenv.2016.11.059
38. Piniewski M, Marcinkowski P, Koskiaho J et al (2019) The effect of sampling frequency and strategy on water quality modelling driven by high-frequency monitoring data in a boreal catchment. J Hydrol 579:124186. https://doi.org/10.1016/j.jhydrol.2019.124186
39. Quesada S, Tena A, Guillén D et al (2014) Dynamics of suspended sediment borne persistent organic pollutants in a large regulated mediterranean river (Ebro, NE Spain). Sci Total Environ 473:381–390. https://doi.org/10.1016/j.scitotenv.2013.11.040
40. QZV Chemie OG (2006) Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Festlegung des Zielzustandes für Oberflächengewässer. https://www.ris.bka.gv.at/eli/bgbl/ii/2006/96/P0/NOR30005066
41. R Core Team (2024) R: A Language and Environment for Statistical Computing. https://www.R-project.org/
42. Schaar H, Zoboli O, Zessner M (2024) Endbericht SimplEstFATE: Modellierung des Verhaltens von Spurenstoffen in der Siedlungswasserwirtschaft. Tech. rep, TU Wien, Vienna, Austria
43. Skeffington RA, Halliday SJ, Wade AJ et al (2015) Using high-frequency water quality data to assess sampling strategies for the EU Water Framework Directive. Hydrol Earth Syst Sci 19(5):2491–2504. https://doi.org/10.5194/hess-19-2491-2015
44. Spycher S, Mangold S, Doppler T et al (2018) Pesticide risks in small streams-how to get as close as possible to the stress imposed on aquatic organisms. Environ Sci Technol 52(8):4526–4535. https://doi.org/10.1021/acs.est.8b00077
45. Stenrød M, Eklo OM, Charnay MP et al (2005) Effect of freezing and thawing on microbial activity and glyphosate degradation in two Norwegian soils. Pest Manag Sci 61(9):887–898. https://doi.org/10.1002/ps.1107
46. Tang A, Zhang X, Li R et al (2022) Spatiotemporal distribution, partitioning behavior and flux of per- and polyfluoroalkyl substances in surface water and sediment from Poyang Lake. China. Chemosphere 295:133855. https://doi.org/10.1016/j.chemosphere.2022.133855
47. Thomas KE, Alexander AC, Chambers PA (2022) Contribution of rain events to surface water loading in 3 watersheds in Canada's Alberta oil sands region. J Hydrol Reg Stud 40:101028. https://doi.org/10.1016/j.ejrh.2022.101028
48. Ulrich H, Macherius A, Kunkel U et al (2024) Novel PFAS-specific monitoring approach for highly impacted surface waters. Chemosphere 349:140893. https://doi.org/10.1016/j.chemosphere.2023.140893
49. Wang J, Bouchez J, Dolant A et al (2024) Sampling frequency, load estimation and the disproportionate effect of storms on solute mass flux in rivers. Sci Total Environ 906:167379. https://doi.org/10.1016/j.scitotenv.2023.167379
50. Wang Z, Walker GW, Muir DCG et al (2020) Toward a global understanding of chemical pollution: a first comprehensive analysis of national and regional chemical inventories. Environ Sci Technol 54(5):2575–2584. https://doi.org/10.1021/acs.est.9b06379
51. Weber N, Lutterbach J, Hufnagl C, et al (2025) Dataset of micropollutant concentrations and standard water quality parameters in surface waters in Austria. https://doi.org/10.48436/RMS5D-YF550
52. Weisner O, Arle J, Liebmann L et al (2022) Three reasons why the water framework directive (WFD) fails to identify pesticide risks. Water Res 208:117848. https://doi.org/10.1016/j.watres.2021.117848
53. Wicke D, Matzinger A, Sonnenberg H et al (2021) Micropollutants in urban stormwater runoff of different land uses. Water 13(9):1312. https://doi.org/10.3390/w13091312
54. Wickham H, Chang W, Henry L et al (2024) ggplot2: Create Elegant Data Visualisations Using the Grammar of Graphics. https://doi.org/10.32614/CRAN.package.ggplot2
55. Winkelbauer A, Fuiko R, Krampe J et al (2014) Crucial elements and technical implementation of intelligent monitoring networks. Water Sci Technol 70(12):1926–1933. https://doi.org/10.2166/wst.2014.415
56. Wittmer I, Junghans. M, Singer H et al (2014) Mikroverunreinigungen – Beurteilungskonzept für organische Spurenstoffe aus diffusen Einträgen. Studie im Auftrag des BAFU. Eawag, Dübendorf, https://www.eawag.ch/fileadmin/Domain1/Abteilungen/uchem/pdf/Wittmer-2014-Mikroverunreinigungen_-_Beurteilungskonzept_fuer_organische-_published_version_.pdf
57. Wolfram J, Stehle S, Bub S et al (2021) Water quality and ecological risks in European surface waters – monitoring improves while water quality decreases. Environ Int 152:106479. https://doi.org/10.1016/j.envint.2021.106479
58. Xiao N, Cook J, Jégousse C et al (2024) ggsci: Scientific Journal and Sci-Fi Themed Color Palettes for 'ggplot2'. https://doi.org/10.32614/CRAN.package.ggsci
59. Yang W, Schmidt C, Wu S et al (2025) Exacerbated anthropogenic water pollution under climate change and urbanization. Water Res 280:123449. https://doi.org/10.1016/j.watres.2025.123449
60. Zoboli O, Clara M, Gabriel O et al (2019) Occurrence and levels of micropollutants across environmental and engineered compartments in Austria. J Environ Manage 232:636–653. https://doi.org/10.1016/j.jenvman.2018.10.074
61. Zoboli O, Weber N, Braun K et al (2024) Systematic underestimation of polycyclic aromatic hydrocarbon aqueous concentrations in rivers. Environ Sci Pollut Res 31(26):38117–38127. https://doi.org/10.1007/s11356-024-33787-9