Survey of Appearance and temporal concentrations of polar organic pollutants in Saxon waters

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ABSTRACT

Integrative passive samplers such as the Chemcatcher are often proposed as alternatives for conventional grab sampling of surface waters. So far, their routine application for regulatory monitoring is hampered (among others) by the fact that TWA concentrations may depend significantly on the design and specifics of the samplers employed. The presented study addresses this issue, focusing on the uptake of polar organic pollutants in three different Chemcatcher configurations and polydimethylsiloxane (PDMS) sheets in the field. Covering waste water treatment plant effluents, creeks, and rivers, samplers were deployed for periods of 14–21 days in eight trials over the course of one year. 33 organic pesticides, 14 transformation products and 31 pharmaceuticals could be detected at least once in TWA concentrations ranging from 0.03 ng/L to 16.5 µg/L. We show that through employing generic, i.e. sampler specific, rather than compound specific sampling rates, the variation among results from three integrative passive sampler designs yields linear correlations with an offset of less than 0.1 and correlation coefficients $r^2 > 0.8$. In this way, TWA concentrations enable the identification of low-concentration xenobiotics of concern, which may support regulatory monitoring correspondingly.

1. Introduction

Anthropogenic pollutants pose the risk of adverse effects in the environment if concentrations exceed toxicologically relevant thresholds [1,2]. Pesticides covering herbicides, insecticides, biocides, and fungicides often enter the environment via spray-drift to nearby surface waters or via field run-off during rain events [3,4]. Active ingredients of pharmaceuticals are mainly introduced through waste water treatment plants (WWTPs) as the compounds are only partly metabolized in humans. This results in direct excretion of biologically active chemicals, as well as active transformation products, in sewage which are commonly not removed by WWTPs [5,6].

In the environment, parent compounds are often converted biotically or abiotically to more polar transformation products (TPs) [7]. For example, the herbicide metolachlor can be biotransformed in soil to metolachlor oxanilic acid (metolachlor OA) and metolachlor 2-oxoethanesulfonic acid (metolachlor ESA) [8]. Transformation may change the ecotoxicological risk that may either increase or decrease [9–11]. Increased polarity of TPs translates into increased mobility in the aquatic environment [10]. Therefore, TPs may remain in the water phase for a longer period of time which could increase their concentration through ongoing emission. Specifically,

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small polar and mobile compounds may accumulate in drinking water reservoirs such as groundwater and water supply dams. This may lead to long-term environmental risks for drinking water safety and has been investigated e.g. for short-chain per- and poly-fluorinated compounds (PFAS) or for highly polar pesticides such as glyphosate [12].

National and international monitoring and assessment plans are implemented such as the European Water Framework Directive (WFD) with its complementary Groundwater Directive to reduce the risk of adverse effects for human consumption, for the environment, and to protect drinking water resources. In this program, selected compounds are monitored in European surface waters and groundwaters, and the results are compared with the annual average Environmental Quality Standards (AA-EQSs) and the maximum allowable concentration (MAC) EQS. Among the monitored compounds are the nonsteroidal anti-inflammatory drug (NSAID) diclofenac, and the herbicides atrazine and terbuthylazine [13]. Generally, grab samples are collected regularly to determine the chemical status, i.e. the concentrations of regulated (groups of) compounds in the water phase.

Averaging grab water concentrations, e.g., over the course of one year do not necessarily regard pollutant fluctuations [14]. Depending on the sampling time (before, during, or after a rain event), the influent and therefore the pollutant burden may differ significantly [14]. Concentration peaks can be monitored by serial sampling over the course of such an event. Provided that maximum and minimum concentrations are covered representatively, average concentrations can be derived from such a sampling profile. Nevertheless, this method leads to an increased number of samples and therefore may elevate costs.

Accordingly, integrative sampling techniques provide a means to overcome such fluctuations. One option is the use of automated integrative samplers. However, these systems are expensive, usually depend on electricity and may not be deployable in remote areas. Passive samplers have been applied as alternatives for periodic grab sampling in many studies [6,15,16]. The advantage of these devices is that analytes are accumulated in the sampler during the whole exposure time, which allows quantification in the low ng/L-range as a time-weighted average [17,18]. Since no external energy source is needed, passive samplers may be placed in almost all environmental settings such as WWTPs [19], remote mountain areas [20], and the open sea [21]. New passive sampler designs are developed frequently [22], but one prominent device is the Chemcatcher passive sampler (CC) developed by Kingston et al. (2000) at the University of Portsmouth, UK [23]. For polar organic pollutants, CC can be equipped with different sampling disks such as the Atlantic HLB-L disk [24], SDB-RPS [17] or SDB-XC disks [25].

To determine time-weighted average concentrations from passive samplers, the sampling rate R_s [L/d] is needed [26,27]. It is a compound-specific parameter specifying how much water volume per day is extracted by the particular sampler. The associated compound concentration in the water, c_w, is related to R_s through its mass collected on the passive sampler m_s [ng] and the sampling time t [d] according to

$$c_w^{twa} = \frac{m_s}{R_s \cdot t}$$ (1)

A serious hindrance for regulatory applications of passive samplers is the uncertainty of R_s and the calculated time-weighted average (TWA) concentrations. In a recently published study we found that an uncertainty of factor 4 in the TWA concentrations must be considered when using a passive sampling approach [28]. This comes mainly from the fact that sampling rates determined in laboratory experiments reflect uptake under field conditions only to a limited extend. Additionally, calibration experiments differ strongly in different studies and laboratories, questioning the comparability of reported R_s values. Therefore, we propose sampler-specific generic sampling rates, taking into account uptake conditions in a variety of experiments and for a large group of compounds. This also accounts for natural variations of environmental concentrations due to inconsistent discharge.

As mentioned above, many different passive samplers have been proposed and new designs are suggested frequently. Commonly, only one sampler configuration is deployed in field studies, hampering the comparability of respective results. In this study, CC passive samplers equipped with three different sorbent disks augmented by polydimethylsiloxane (PDMS) sheets were deployed at eight Saxon field sites: three WWTPs, three small streams, and two rivers. The goal was to test the comparability of different passive samplers in field settings, and to investigate temporal patterns and changes of selected polar pesticides and pharmaceuticals. Generic sampling rates were used to calculate TWA concentrations that were compared with environmental threshold concentrations such as EQSs and regulatory acceptable concentrations (RACs).

2. Material and methods

Three different passive samplers (Atlantic HLB-L disks, Attract SDB-RPS disks and Attract SDB-XC disks) were exposed during the field sampling campaign. Passive samplers were deployed in cages to protect them from debris. In the small streams, samplers were fastened on meshes and placed shortly above the sediment. Trip blanks were used to monitor contamination during transport (to and from the sampling site), storage, and extraction. During the deployment of the samplers in the field the trip blanks were stored at 4 °C in the laboratory. In the laboratory they were extracted parallel to the corresponding field samples. Each sampler type got a trip blank for each sampling site. Quantification was performed with an internal calibration with solvent standards ranging from 0.1 ng/mL to 1000 ng/mL. No significant concentrations could be determined in the blanks.

Passive samplers were always deployed in duplicates at all sites. In total, 128 Chemcatchers equipped with hydrophilic lipophilic balance (CC-HLB) and styrene divinyl benzene (CC-XC), and 112 polydimethylsiloxane samplers were deployed. Chemcatchers equipped with styrene divinylbenzene reversed phase sulfonate (CC-RPS) were deployed at two sites (WWTP Groβbardau and Parthe), yielding a total of 36 samplers.
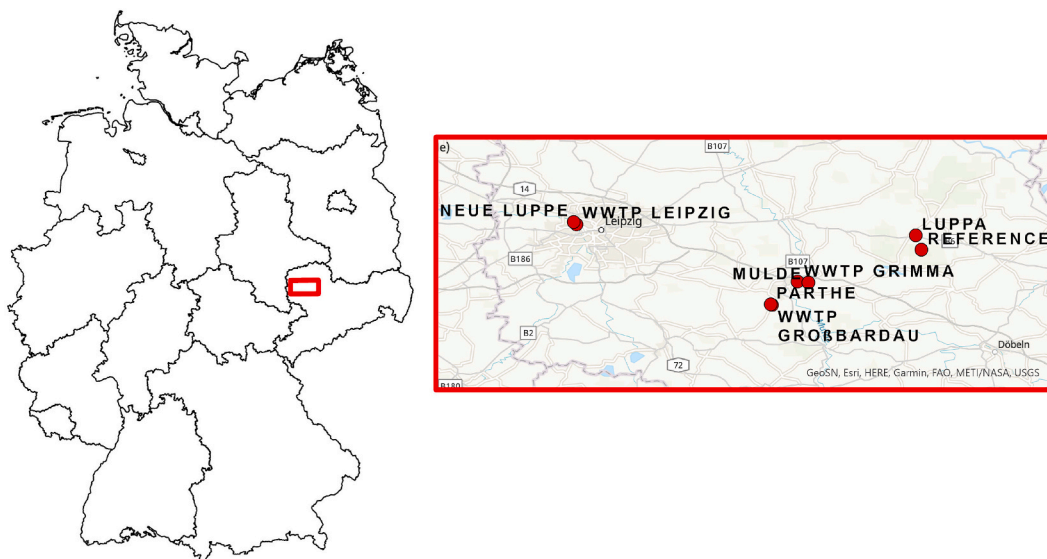
Fig. 1. Geographic position of sampling sites of the field study in the State of Saxony in Germany. (WWTP: Waste water treatment plant). Duplicates were deployed at each site for eight samling periods.

2.1. Sampling sites

Field trials were conducted at eight sites in Saxony. Three effluents of WWTPs treatment plants were included: The WWTP in Leipzig (51.3560 N/12.3400 E) clearing 750,000 population equivalents per day, the WWTP in Grimma (51.2496 N/12.7511 E) clearing 25,000 population equivalents per day, and the WWTP in Großbardau (51.2066 N/12.7037 E) clearing 1500 population equivalents per day. All WWTPs use the common three clearing steps (i) mechanical treatment followed by (ii) biological treatment of the waste water, and (iii) removal of phosphate. These sites were selected because WWTPs are known point sources for input of anthropogenic contaminants in surface waters [29]. Additionally, samplers were deployed at the small streams Luppa (51.3353 N/12.9714 E), Altenhainer Bach (51.3087 N/12.9815 E), and Parthe (51.2074 N/12.7014 E), and the rivers Mulde (51.2481 N/12.7716 E) and Neue Luppe (51.3605 N/12.3347 E, Fig. 1). The sites Parthe, Mulde, and Neue Luppe receive the effluents of the respective WWTPs (Fig. 1).

The site Altenhainer Bach was chosen as reference site, since it only receives waters from a forest without direct input of field run-off. The site dried out during the sampling campaign in the summer, so no reference data are available for that period. The site Luppa mainly receives agricultural effluents because it is surrounded by fields and some cattle. Upstream of the site lies the small village Luppa, possibly yielding additional urban influence on the sampling site. The small stream Parthe also receives field run-off. Moreover, this sampling site receives cleared waste water from the WWTP Großbardau 50 m upstream of the sampling site.

The river Mulde receives the cleared waste water from the WWTP in Grimma, and thus is subject to urban impact. The catchment area covers a larger part of Saxony. Besides the city of Grimma, river Mulde is mainly surrounded by smaller settlements and agricultural land. The respective sampling site was located 2.5 km downstream of the WWTP Grimma. Closer proximity to this point source was not possible due to the local road network. The site Neue Luppe is an artificial stream running parallel to its natural predecessor, the river Weiße Elster. The latter drains a flood basin which runs through the city of Leipzig and is therefore strongly impacted by urban run-off. The sampling site was located 250 m downstream of the effluent of the WWTP Leipzig.

Samplers were deployed for eight trials spreading the year 2020. In February, March, April, and May samplers were deployed for three weeks and in July, August, October and November for two weeks. The exposure time was decreased from 21 days to 14 days in the second half of the campaign to reduce the logistic effort. Repeated sampling at the same sites was applied to enable detecting temporal changes of the analyzed pesticides, pharmaceuticals, and transformation products.

2.2. Passive sampler preparation and extraction

Chemcatchers were prepared as described in the electronic supplementary material (ESI). Briefly, extraction disks were conditioned before deployment using methanol and bidistilled water. Clean and dry Chemcatcher bodies (version 3, AT Engineering Technologies, Tadley/UK) were covered with an extraction disk and a PES (polyether sulfone) diffusion limiting membrane (0.45 μm, Pall). Samplers were deployed in duplicates at all sampling sites. After deployment, Chemcatchers were disassembled and the disks were stored frozen until extraction. PES membranes were discarded (sorption to PES was tested in different laboratory studies). The CC-disks were extracted sequentially with two organic solvents and the combined extracts were evaporated to a final volume of 1 mL under a nitrogen stream using a graduated Kurdena-Danish tube. Samples were stored at −20 °C until analysis. A detailed description of the extraction procedure can be found in the ESI (SM-1).

Table 1
Generic sampling rates in L/d applied in this study from Römerscheid et al. (2023).

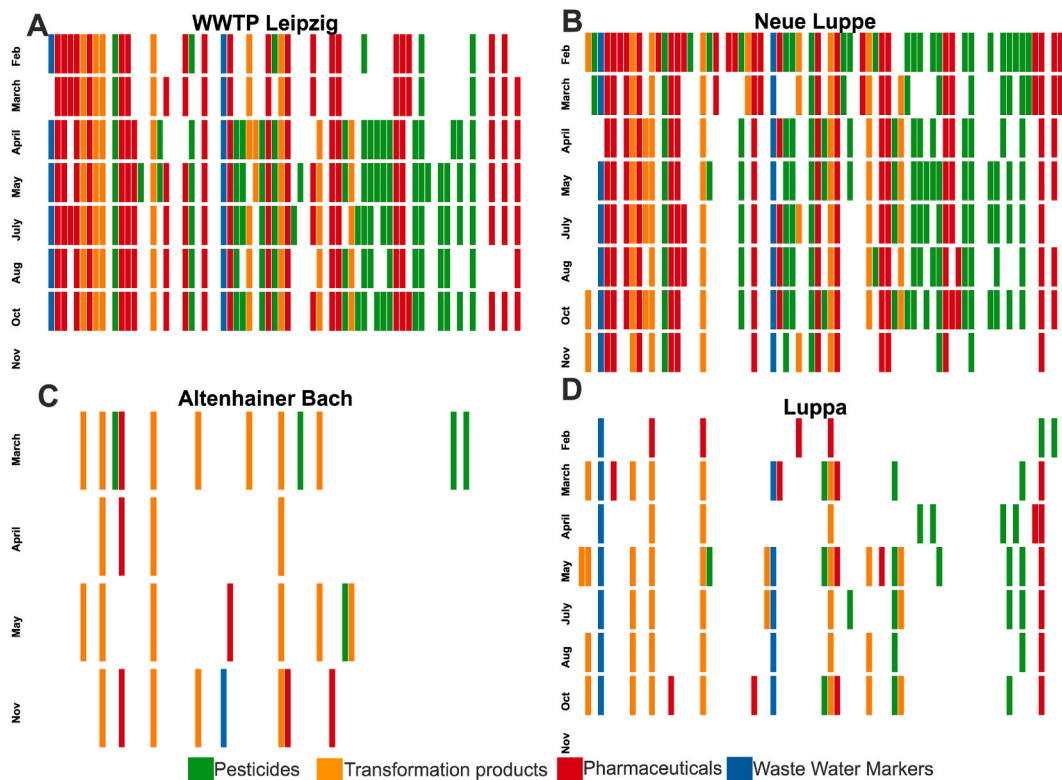| Sampler	generic Rs	lower limit	upper limit
CC-HLB	0.047	0.028	0.078
CC-RPS	0.100	0.030	0.198
CC-XC	0.126	0.022	0.265

Fig. 2. Barcode plot of compounds detected in CC-HLB (Chemcatcher equipped with Atlantic HLB disk) at the sites WWTP (waste water treatment plant) Leipzig (panel A) Neue Luppe (panel B), Altenhainer Bach (panel C) and Luppa (panel D). Each bar represents a positive detection. Due to urban run-off (e.g. from roads) more compounds can be detected at the site Neue Luppe compared to the WWTP effluent. Compounds which are only detected in the WWTP effluent are probably diluted below the limit of detection at the site Neue Luppe. Compared to the urban sampling sites, Altenhainer Bach and Luppa (rural locations) contained a lower contaminant burden in terms of detected compounds. Additionally, transformation products make up a higher fraction than at the urban sites. Empty rows indicate that only one sampler was retrieved and therefore not evaluated.

PDMS sheets were cut in pieces of 1 cm × 5.5 cm. As we noted that such small pieces accumulate only very little amounts of analytes, the sampler size was increased to 5.5 cm × 5.5 cm after the fourth sampling campaign in June. The sheets were precleaned via Soxhlet extraction with ethyl acetate for 40 h to remove oligomers [30]. Subsequently, the samplers were rinsed with and stored in methanol.

After exposure, samplers were frozen in glass vials until extraction. PDMS sheets were extracted twice with 15 mL methanol each. Internal standard was added to the combined extracts and samples were evaporated to a final volume of 0.5 mL. All sampler extracts were analyzed with HPLC-MS/MS using methods described in the ESI.

2.3. Determination of aqueous concentrations from passive sampler

If both duplicates could be retrieved from the field, the mean m_s was calculated. Generic sampling rates as introduced by Römerscheid et al. (2023) were applied in this study to determine TWA concentrations from different Chemcatcher designs. 0.126 L/d, 0.047 L/d and 0.100 L/d were used as a sampling rate for CC-XC, C-HLB, and CC-RPS, respectively (Table 1). Uncertainty of TWA concentrations was determined from 10 % quantile and 90 % quantile as discussed in Römerscheid et al. [28]

Aqueous concentrations from PDMS sheets were derived by sampler-water partition coefficients. A detailed description of the experiment and the applied sampler-water partition coefficients can be found in the ESI SM-1 and Tables SM–1.
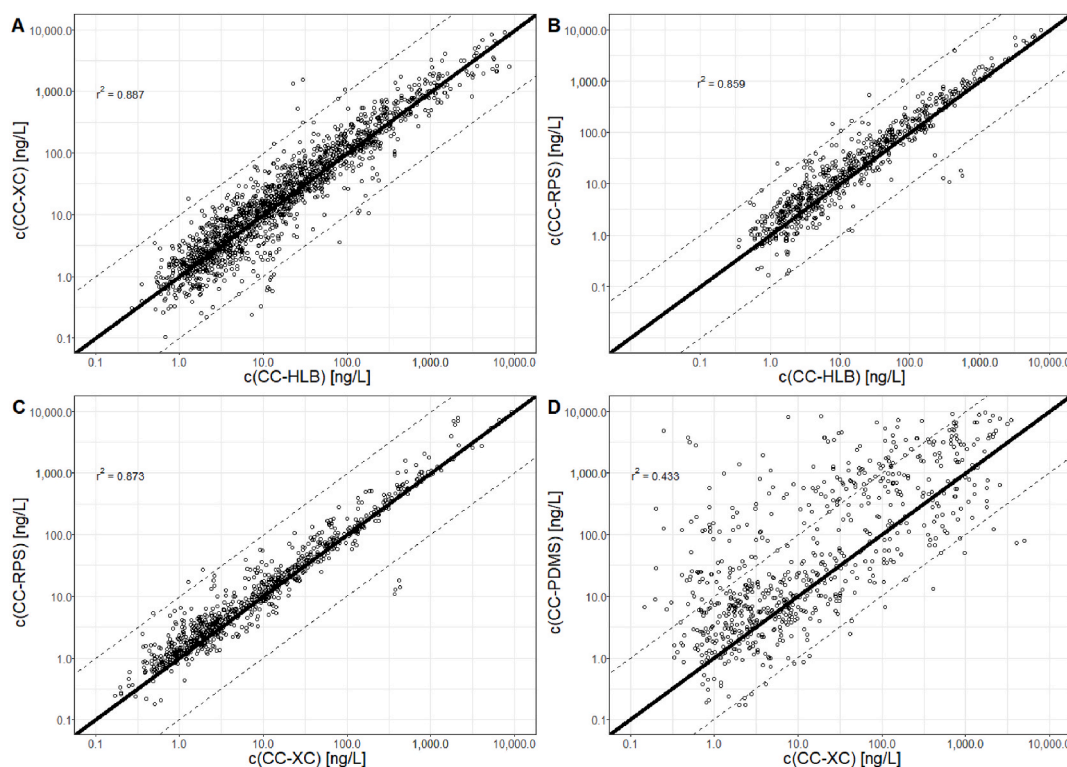
Fig. 3. Selected correlation of c_w derived for the different samplers deployed in the field trials. The bold line represents the 1:1-relationship and the dashed lines the 10:1- and 1:10-relationships.

3. Results and discussion

3.1. Accumulation of polar organic compounds in different passive samplers

78 compounds could be detected in field samples. Most analytes were detected in the river Neue Luppe. Similar compound patterns can be found in the WWTPs and their receiving water courses, e.g. for the sites Neue Luppe and WWTP Leipzig (Fig. 2 A and B). Each bar in the barcode plot represents the detection of one compound. Some compounds can only be detected in the WWTP's effluent due to their dilution below the detection limit in the receiving water bodies. Sorption to organic matter may also play a role as a sink for compounds. However, this is more relevant for nonpolar organic pollutants, because these tend to sorb stronger to organic matter [31]. Fewest compounds were detected at the reference site Altenhainer Bach and in the small stream Luppa (Fig. 2C and D). At both sites, 75 % of positive detections are pesticides and their transformation products. At the sites Parthe and Mulde, 64 % and 60 % of positive detections are pesticides and TPs, respectively. At the other sites, the fraction of pesticides and TPs ranges from 55 % to 58 %. In the standard mix used for the target screening, this fraction of pesticides and TPs is 60 %. Therefore, pesticides fraction reflects the agricultural influence on the sampling sites. The more widespread distribution of pesticides compared to pharmaceuticals can be attributed to the increased diffusive input in water bodies. This reflects their broad application in both rural and urban environments as well as the deposition of airborne pesticide residues proven to be ubiquitous in Germany [32].

Time-weighted average (TWA) concentrations in different passive samplers are plotted in Fig. 3. The correlation of the concentrations in CC-XC (Chemcatcher equipped with Attract SDB-XC disk) and CC-HLB (Chemcatcher equipped with Atlantic HLB-L disk) is displayed in panel A. Data lie slightly above the 1:1-line, which means that TWA concentrations derived by CC-XC are slightly larger than TWA concentrations derived by CC-HLB. Data correlate well with the equation log CC-XC = 0.06($\pm$0.01) + 0.99($\pm$0.01) log CC-HLB (r^2 = 0.890 and *se* (standard error) = 0.30). This shows that the application of generic sampling rates makes data from different passive samplers comparable. Figure SM-1 (panel A) shows the correlation of ng/disk for CC-HLB and CC-XC. Here, most data lie above the 1:1-line. Still, the data correlate well with the equation log CC-XC = 0.49($\pm$0.01) + 0.99($\pm$0.01) log CC-HLB (r^2 = 0.890 and se (standard error) = 0.30). The offset shows that the concentrations in CC-XC are on average half an order of magnitude larger than concentrations in CC-HLB. The compounds below the 1:1-line are mainly pesticide TPs (methyldephenylchloridazon (MDP-CDZ), dephenyl chloridazon (DP-CDZ), and dimethachlor OA). All these compounds are very polar with log K_{ow} < 1, which shows that CC-XC is less suitable for sampling such compounds. This can be attributed to the fact that CC-HLB consists of poly(divinylbenzene-*co*-vinylpyrrolidone) as a receiving phase, which contains more polar functional groups than poly(styrene-divinylbenzene) (receiving phase in SDB-XC). Hence, more polar organic compounds such as transformation products are retained better in CC-HLB.
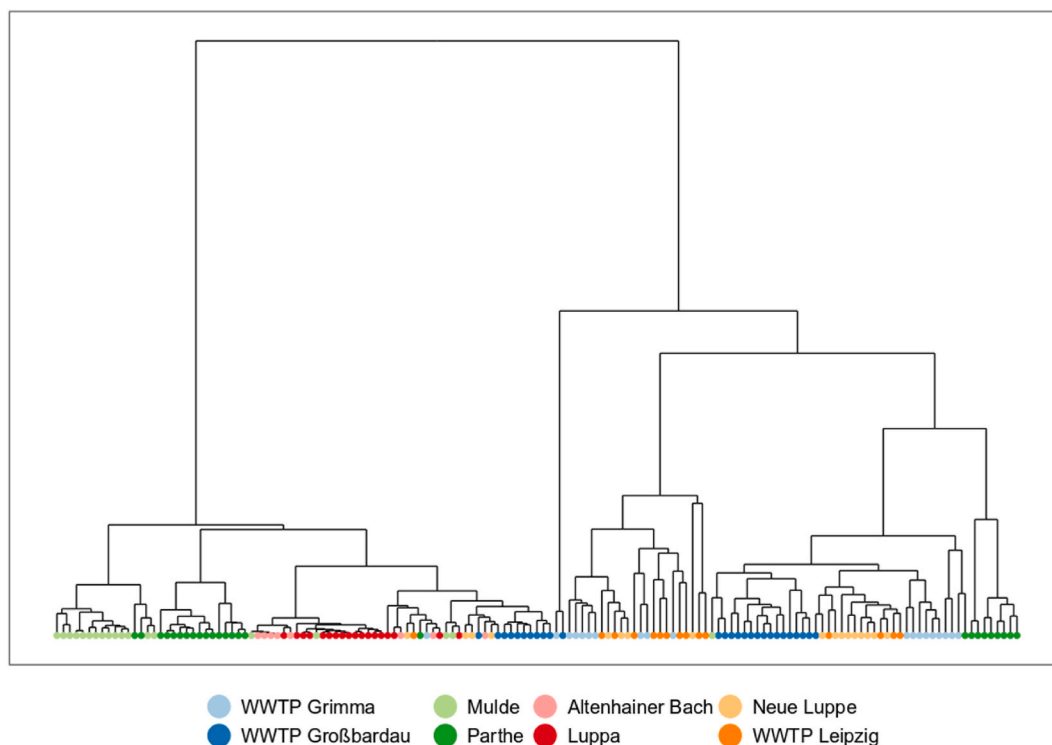
Fig. 4. Hierarchical cluster analysis of field samples without PDMS samplers, sorted by sampling site. WWTP: Waste water treatment plant.

The correlation between CC-HLB and CC-RPS (Chemcatcher equipped with Attract SDB-RPS disk, Fig. 3, panel B) is as good as the correlation between *C*C-HLB and CC-XC with the equation log CC-RPS $= 0.17(\pm0.02) + 0.97(\pm0.01)$ log CC-HLB ($r^2 = 0.883$ and se $= 0.31$). In Figure SM-1, oxcarbazepine is an outlier, which is accumulated in higher masses in CC-HLB compared to CC-RPS. This outlier can also be found in panel C (Figure SM-1), which displays the correlation between CC-XC and CC-RPS. A comparison of concentration in the CC-XC and the CC-RPS disk via the Wilcoxon-test showed that the concentration differences in both samplers are statistically insignificant. Chemically, the sampling phases are very similar, as SDB-RPS contains reversed phase sulfonate moieties additionally to the styrene-divinyl benzene backbone. However, the similar uptake of polar analytes in field trials shows that the chemical difference is not a main contributor to uptake uncertainty between these two sampler designs.

The comparison of masses in different passive samplers shows that masses in CC-HLB are generally 0.4 log units lower than concentrations in CC-XC or CC-RPS disks. In field applications, *C*C-RPS accumulates polar organic compounds in a similar manner as CC-XC, though laboratory calibrations suggest that CC-RPS is more suitable for polar compounds than CC-XC (e.g. Table 1). Larger differences were observed for oxcarbazepine, which reaches saturation within days for CC-RPS in laboratory experiments. The mass accumulated by two passive samplers of the same type exposed in parallel has a mean deviation of 18 %, which usually corresponds to deviations of less than 10 ng/disk. Therefore, the mass differences in the duplicates are not the main determinate of the uncertainty. This overview shows that integrative passive samplers generally yield comparable results in field applications, although laboratory studies often show larger differences in their sampling behavior. The application of generic sampling rates allows for comparison of different sampler types, as differences in m_s are compensated. This can also be seen in Fig. 3 and Figure SM-1.

Equilibrium sampling was conducted with PDMS sheets. The resulting concentrations differ significantly from the concentrations derived by integrative sampling (Fig. 3, panel D), which could be confirmed by hierarchical cluster analysis (HCA). Briefly, the Euclidian distance of scaled samples is determined. Subsequently, samples are sorted so that samples with low distances (i.e., similar contamination patterns) are grouped together. Fig. 4 and Figure SM-2 display the results of hierarchical cluster with and without PDMS. If PDMS samplers are included in the clustering, the groups can be roughly differentiated in integrative and equilibrium passive samplers (Fig SM-2). A likely reason is that time-integrative samplers are optimized to extract even small analyte concentrations, with elimination kinetics too slow to reach chemical equilibrium within typical exposure times. By contrast, equilibrium samplers are optimized for fast uptake and elimination, with a possibly lower sensitivity for analytes at the low concentration end. Partition data determined by our group show that PDMS reaches equilibrium for the selected analytes within few days, which is also in line with a study conducted by Wille et al. (2011) [33]. Therefore, the silicon sheets display the water concentration in the days before sampler retrieval while the Chemcatcher designs represent the TWA for the total exposure time. The increase of PDMS sampler size in July 2020 shows that larger sampler concentrations could be achieved in the last three sampling campaigns (Figure SM-3). However, the total number of positive detections could not be increased. Note further that the number of analytes detected by the equilibrated PDMS is lower than with the Chemcatchers in kinetic uptake mode, demonstrating the superiority of latter samplers regarding
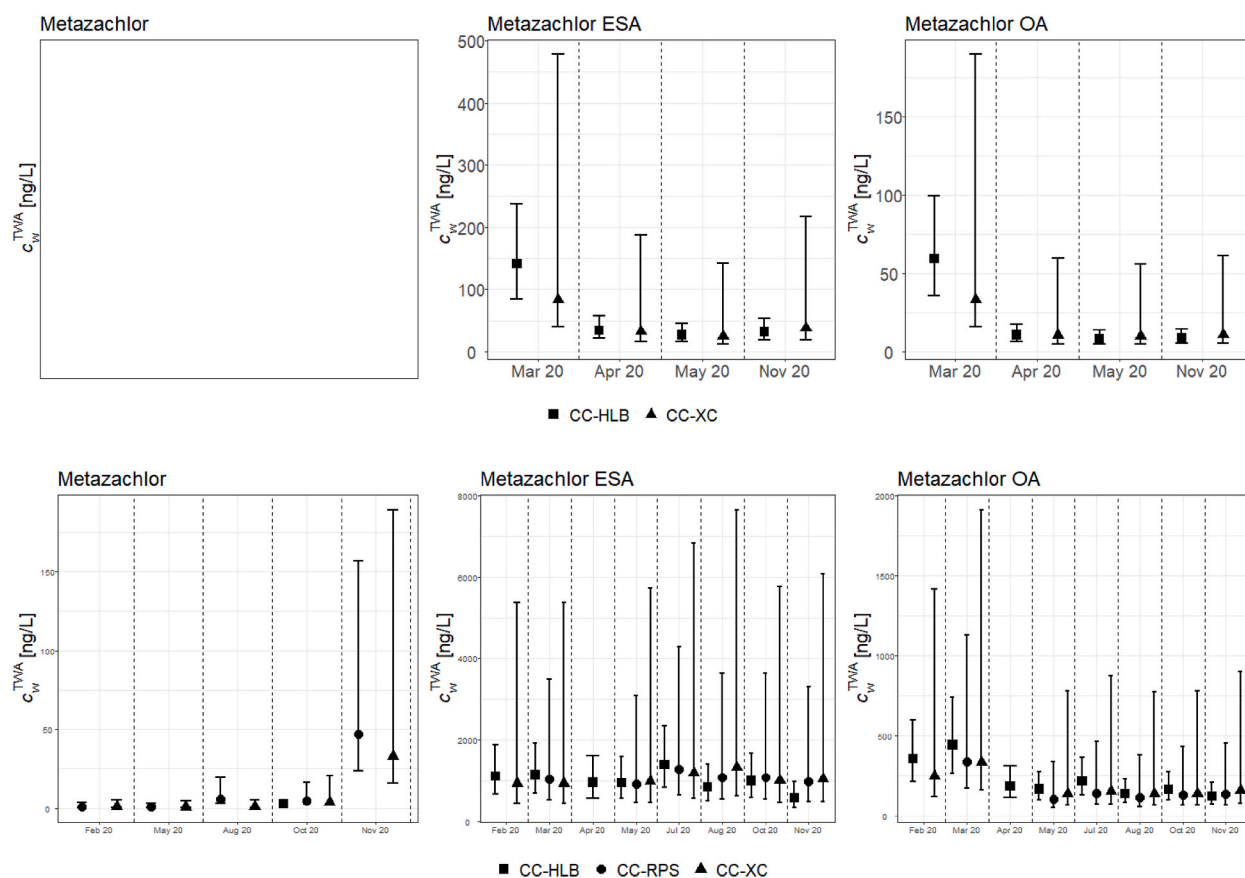
Fig. 5. Changes in metazachlor concentrations and its OA and ESA transformation product at the sites Altenhainer Bach (top) and Parthe (bottom). Metazachlor was not detected in Altenhainer Bach, which is why the top left panel is empty. TWA concentrations were derived from generic sampling rates (Table 1). Error bars represent uncertainty of generic sampling rates.

low-concentration analytes (see above). Here, prominent examples are caffeine, trimethoprim, and diclofenac with mean TWA concentrations of 51 ng/L, 130 ng/L and 6351 ng/L as opposed to their non-detection by the PDMS sampler at the site WWTP Leipzig (see Tables SM–7 to SM-10). However, in different study designs and e.g. when discussing biological uptake PDMS gives valuable comprehensive information to the applied Chemcatchers [33].

Exclusion of PDMS reveals site-specific clustering for integrative passive samplers (Fig. 4). The top branches contain sites that are distinguished by increased concentrations of pharmaceuticals (right) and sites mainly influenced by pesticides (left). The right branch contains most samples from WWTPs and Neue Luppe as well as some samples from the site Parthe. By contrast, the left group contains most samples from the sites Mulde, Luppa, Altenhainer Bach and other samples from Parthe, and interestingly also the WWTP Groβbardau. Accordingly, HCA discriminates predominant urban impact (pharmaceuticals) from predominant agricultural impact (pesticides and their TPs), illustrating a way of profiling aqueous contamination through time-integrative passive sampling.

Samples from Altenhainer Bach and Luppa generally cluster together, which is in line with the contamination patterns discussed above. The Parthe samplers clustering in the pharmaceuticals group were deployed in winter time (February, March, November). This shows conversely that the application of pesticides near this sampling sites significantly shifts the contamination pattern during the summer months.

3.2. Pesticides and metabolites in saxon surface waters

TWA concentrations are determined using generic sampling rates derived from different studies in our laboratory and literature data (ESI SM-1.2, Römerscheid et al. [28], section 2.3). Error bars represent the 10 % and 90 % quantile of combined literature data and laboratory studies. Therefore, the uncertainties are relatively large. The mean value was used as a threshold mark to discuss exceedances of regulatory acceptable concentrations (RACs) and environmental quality standards (EQSs) in the next section.

Pesticides were detected at all sampling sites. Lowest concentrations were found at the reference site Altenhainer Bach, while the highest concentrations were found in the WWTP in Leipzig and in the river Neue Luppe. The fewest compounds were also detected at the reference site. This shows that this site is comparatively unaffected by anthropogenic input since the concentrations of the detected compounds were generally lower than the concentrations at the other sampling sites.
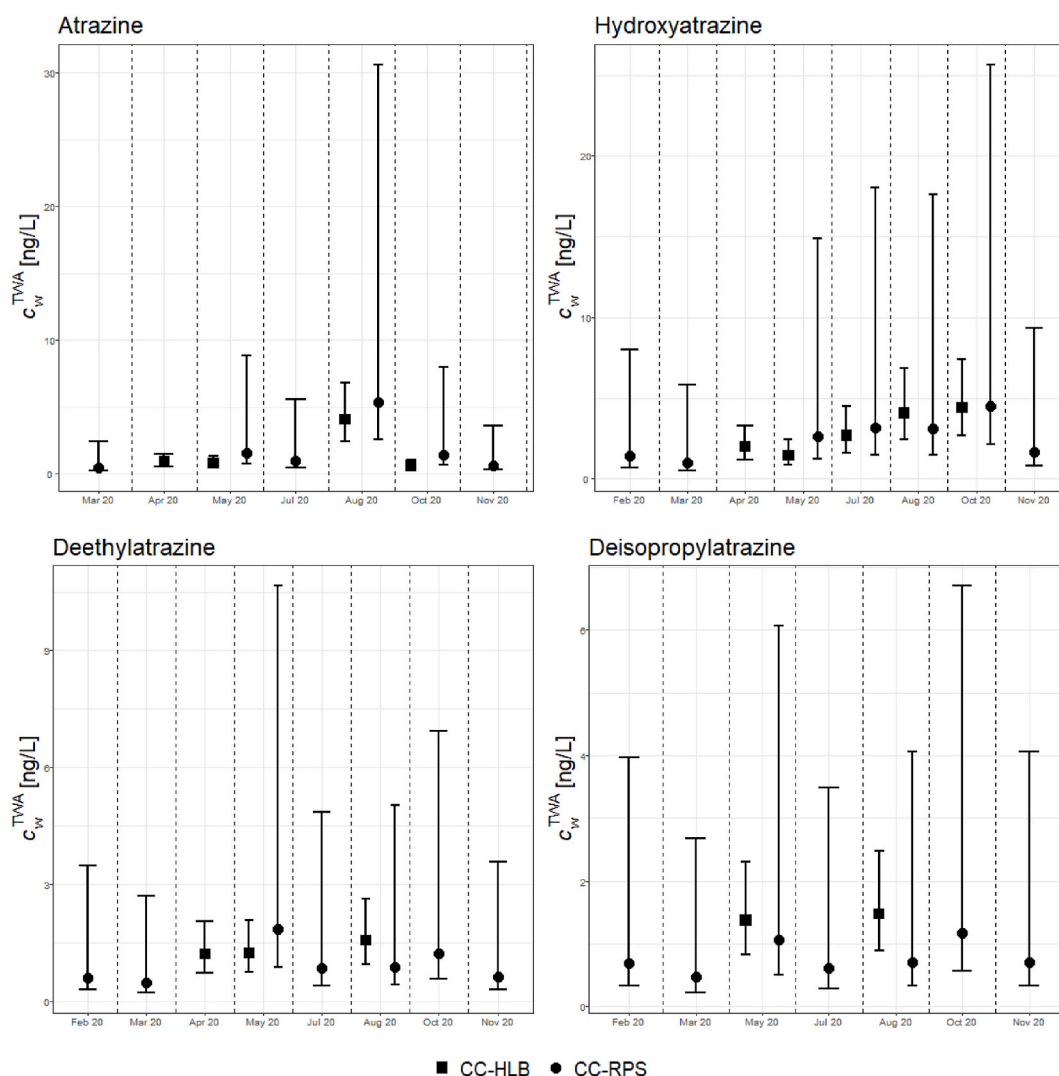
Fig. 6. Changes of time-weighted average concentrations of atrazine and its transformation products hydroxyatrazine (OH-ATZ), deethylatrazine (DE-ATZ) and deisopropylatrazine (DIP-ATZ) at the site Mulde. TWA concentrations were derived from generic sampling rates (Table 1). Error bars represent uncertainty of generic sampling rates.

The pesticide transformation product (TP) metazachlor 2-oxoethanesulfonic acid (MTZ-ESA) was detected at all sampling sites, in concentrations up to 150 ng/L in March 2020 in Altenhainer Bach. The concentration decreased below 50 ng/L in November 2020. A similar trend can be observed for the pesticide TPs metazachlor oxanilic acid (MTZ-OA), metolachlor ESA (MTL-ESA), and metolachlor OA (MTL-OA), though their maximum concentrations are below that of MTZ-ESA (Fig. 5, top).

Both metazachlor and metolachlor have only short half-lives in soils, which leads to excessive findings of their TPs in agricultural catchments, groundwater wells, and even in drinking water wells [10]. Ulrich et al. (2021) could show that while metazachlor could only be detected four weeks after the application, the OA and ESA TPs were repeatedly detected over the course of two months, especially after rain events [10]. There are no known input sources upstream of the sampling site since it is a landscape conservation area, where application of pesticides is generally prohibited. Therefore, spray-drift from nearby fields is a reasonable source of the detected pesticides. A corresponding spray-drift origin is likely to hold also for the herbicide glyphosate that was found in forest soils near application sites in Brasil [34]. Also deposition of airborne pesticide residues cannot be excluded [32].

The highest MTZ-ESA concentrations were detected in the small stream Parthe (Fig. 5, bottom). All deployed passive samplers detected this TP in TWA concentrations between 1000 ng/L to 1500 ng/L with a slight decrease during the second half of the sampling campaign. At the site Luppa, the TWA concentrations of MTZ-ESA are fairly constant during the course of the sampling campaign, but the concentrations are lower than in the Parthe, ranging from 200 ng/L to 400 ng/L. Towards the end of the sampling campaign, the concentration seems to drop slightly. TWA concentrations of MTZ-ESA in the WWTPs are fairly constant in Grimma and Leipzig, ranging from 100 ng/L to 200 ng/L. Concentrations in the WWTP Großbardau reach a peak concentration in July but are otherwise in a similar magnitude as the WWTPs in Grimma and Leipzig.

The TWA concentration of the parent compound metazachlor (MTZ) is generally at least a factor of 10 below the concentration of its ESA TP. Highest TWA concentrations (47 ng/L) could be observed in November at the Parthe with CC-RPS, while MTZ could not be detected at the sites Luppa and Altenhainer Bach. As a pre-emergence herbicide, MTZ is generally applied before weeds can grow on the field. An application peak can be observed at river Mulde in November when the concentration was more than twice as high as at other sampling times. The detected concentration of 4.9 ng/L in CC-HLB is comparable to concentrations detected at the same site in 2018 (4.0 ng/L) [24].

The TWA concentration pattern of the TP MTZ-OA is similar to the one of MTZ- ESA, but after application peaks the concentration decreases slightly faster: At the site Mulde, a peak can be observed for metazachlor ESA and OA in March 2020 (Tables SM–7 to SM-10). After one month, the concentration of MTZ-OA is reduced to 1/4, while the concentration of MTZ-ESA remained nearly constant. The fast decrease of metazachlor and metazachlor OA is in line with investigations by Ulrich et al. (2021) [10]. The detected concentrations of metazachlor are also comparable to data obtained by Tauchnitz et al. (2020), who detected up to 30 ng/L of the herbicide in the Querne/Weida catchment in Saxony-Anhalt. At urban sites, the detected maximum concentration of metazachlor was slightly lower (20 ng/L) [35]. MTZ-ESA could be detected in the river Danube in Hungary in similar concentrations as at the sites Neue Luppe and Mulde [36].

Though application of atrazine (ATZ) has been forbidden in Germany since 1991 and in the European Union since 2003, this herbicide could still be detected at all sampling sites except for the reference site. The associated TPs deethylatrazine, hydroxyatrazine, and deisopropylatrazine were detected at all sampling sites as well. TWA concentrations were generally below 10 ng/L. All detected TWA concentrations are far below the EQS of 600 ng/L [37]. ATZ input in 2020 was fairly constant at all sampling sites, except for the site Mulde (Fig. 6). Here, TWA concentrations increased from February (not detected) to May (0.8 ng/L in CC-HLB and 1.5 ng/L in CC-XC), remained relatively constant in July (0.7 ng/L in CC-HLB and 1.0 ng/L in CC-XC) and increased significantly in August (4.2 ng/L in CC-HLB and 5.9 ng/L in CC-XC).

While the TWA concentration of ATZ drops in October, the TWA concentration of its TP hydroxy atrazine (OH-ATZ) is still elevated. Possibly, the concentration peak of OH-ATZ occurred between the sampling in August and October. Compared to atrazine the TWA concentration of OH-ATZ is generally larger. The compound could be detected at all sampling sites including the reference site in concentrations up to 16 ng/L in the effluent of WWTP Leipzig (CC-HLB). Higher concentrations (25 ng/L) were detected with CC-HLB in February at the site Neue Luppe, but the accumulated mass differentiates strongly in the duplicates (15 ng/disk vs. 34 ng/disk), which makes the result relatively uncertain. Such considerable deviations in duplicates are the exception, but to verify concentrations it is generally proposed to deploy replicates of passive samplers [38].

The atrazine TPs deethylatrazine (DE-ATZ) and deisopropylatrazine (DIP-ATZ) could be detected in comparable concentrations as the parent compound (up to 2 ng/L). At the site Mulde TWA concentrations of DE-ATZ follow the same pattern as ATZ. TWA concentrations peak in May and in August, but changes are not as strong as for the ATZ concentration. In fact, considering the standard deviations of the detected concentrations changes are insignificant. The same applies to DIP-ATZ. Interestingly, the concentration of this compound increases from August to October. This may be related to a slower transformation compared to DE-ATZ and OH-ATZ.

It is possible that the background ATZ concentration is related to leaching from soils or shallow ground water, since the input is relatively constant [39,40]. However, the increased TWA concentration in August suggests recent input. This is also supported by the fact that the deethylatrazine-to-atrazine ratio (DAR) decreased from 1.3 in July to 0.4 in August. This ratio was suggested to distinguish atrazine input from point sources and diffuse sources [40,41]. At the other sampling sites, DARs do not drop below 0.8, characterizing atrazine levels at those sites as generally resulting from diffusive input. It is notable that CC-HLB fails to detect atrazine at the sites Neue Luppe and WWTP Leipzig due to too low concentrations, while CC-XC can still detect the compound.

The neonicotinoid insecticides imidacloprid, clothianidin, thiacloprid, and thiamethoxam have been banned for use in the European Union in 2018 due to adverse effects on bee populations. Therefore, the approval expired on January 31, 2019, December 01, 2020, February 03, 2020, and April 30, 2019 for clothiadin, imidacloprid, thiacloprid, and thiamethoxam, respectively [37]. The disapproval was followed by a period of several months where rests of the pesticides could still be applied. These periods of application ended between December 2019 (clothianidin) and October 2020 (thiacloprid). The application of imidacloprid in some products was still legal in Germany until June 2022 [42].

Neonicotinoids are characterized by very low RAC values ranging from 4 ng/L for thiacloprid to 43 ng/L for thiamethoxam due to adverse effects on e.g. bee populations. Clothianidin was detected only two times during the sampling campaign, in the small stream Parthe in February 2020 (1.7 ng/L) and in the river Neue Luppe (8.8 ng/L). Thiamethoxam was detected at seven sampling sites, including the reference site in concentrations below the RAC value (highest concentration: 9.3 ng/L, Neue Luppe in January). It is notable that the compound was only found until the summer of 2020 in generally decreasing concentrations, which suggests only punctual inputs. By contrast, imidacloprid and thiacloprid could be detected at all sampling sites. Again, the maximum concentrations of thiacloprid were detected in January at the site Neue Luppe (12 ng/L). At the other sampling times the concentration did not exceed 2.5 ng/L. In the WWTPs the highest concentrations of thiacloprid were also measured in January, decreasing over the course of the study. At the receiving water course Parthe, the thiacloprid concentration remains relatively constant when measured, ranging from 0.2 ng/L to 0.4 ng/L. At the site Mulde, an application peak can be found in May 2020, after which the concentration decreases below the detection limit until October 2020. At the sites Luppa and Altenhainer Bach, thiacloprid was only detected once in May 2020 in concentrations below 1 ng/L. Though the approval expired in early 2020, application of thiacloprid plant protection agents was still legal in Germany until February 2021.

Imidacloprid could be detected in concentrations above the RAC value (9 ng/L) in all WWTP effluents and in the Neue Luppe. The compound was detected at all sampling sites, including the reference site in spring. The detections reflect the end of the application period for the different neonicotinoids: While clothianidin and thiamethoxam were detected only scarcely, thiacloprid and
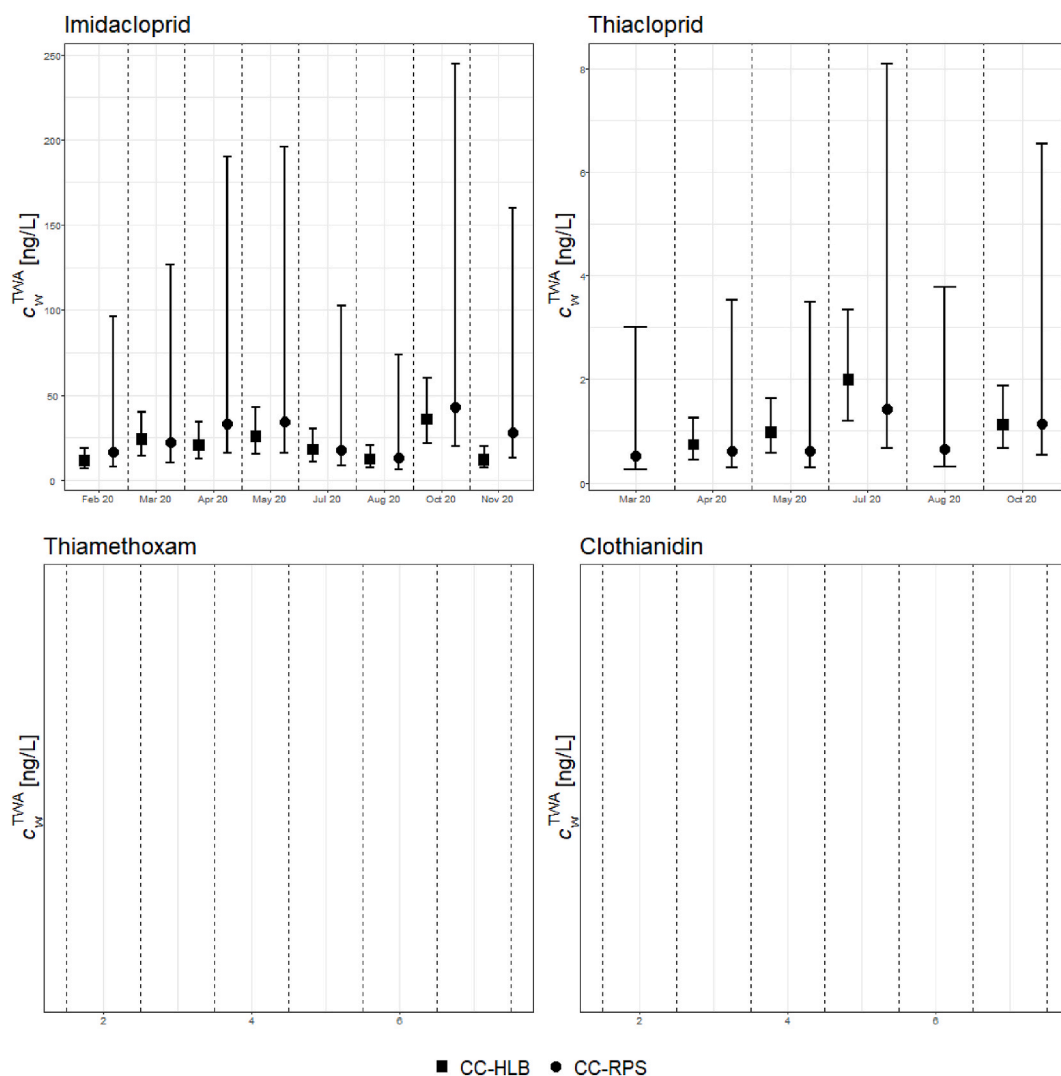
Fig. 7. Changes of time-weighted average concentrations of the neonicotinoid insecticides imidacloprid, thiacloprid, thiamethoxam and clothianidin at the site WWTP Grimma. TWA concentrations were derived from generic sampling rates (Table 1). Error bars represent uncertainty of generic sampling rates.

imidacloprid, whose application was still legal during the whole sampling campaign, were detected in higher frequencies and concentrations. It is possible that the concentrations will slowly start sinking in the next years. Münze et al. (2017) reported mean concentrations of 36 ng/L imidacloprid in streams in Saxony-Anhalt downstream of WWTP effluents [43]. This is slightly higher than concentrations reported in this study and might be attributed to the fact that the amount of products available steadily decreased in the last years [42].

Besides integrative passive samplers, PDMS sheets were deployed in the sampling campaign in 2020. Due to the low capacity of these nonpolar passive samplers, 90 % of detected concentrations were below 21 ng/sampler. The number of detections was much lower in PDMS compared to e.g. Atlantic HLB-L (1288 detections and 2572 detections, respectively). Only 18 % of positive detections in PDMS were larger than 10 ng/sampler, while more than 40 % of positive detections in Atlantic HLB-L were larger than 10 ng/sampler. This shows that the capacity of the Chemcatchers is much larger for polar and semipolar organic compounds compared to PDMS. It could be increased by upscaling the deployed samplers. As discussed above, this equilibrium sampler yields typically (too) low sensitivities for polar analytes due to their low PDMS-water partition coefficients. Therefore, the data are not discussed more detailed here.

3.3. Pharmaceuticals and markers

The overall largest concentrations were detected in the WWTP effluents and at the site Neue Luppe for the compounds benzotriazole and diclofenac. The German Environmental Agency classifies diclofenac as a prioritized pharmaceutical since it is found in
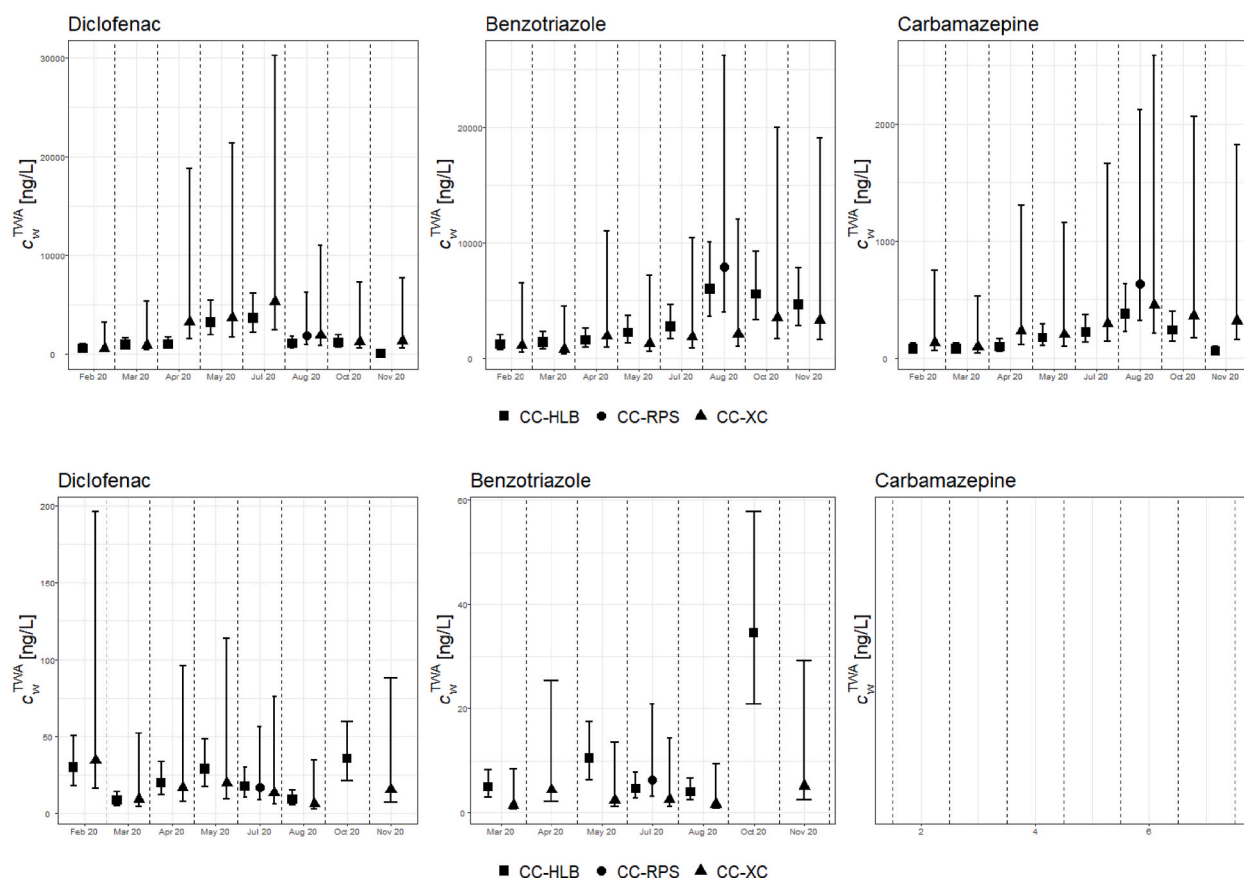
Fig. 8. TWA concentrations of selected pharmaceuticals at the sites Neue Luppe (top) and Luppa (bottom). Carbamazepine could not be detected at the site Luppa. TWA concentrations were derived from generic sampling rates (Table 1). Error bars represent uncertainty of generic sampling rates.

concentrations above 1 µg/L in German surface waters [44]. The compound is known to cause adverse effects, e.g., in vultures since the early 1990s. 85 t of the compound are consumed in Germany every year [45].

The highest concentration of diclofenac was measured in the effluent of the WWTP Leipzig (15 µg/L). In the other WWTP effluents, concentrations above 10 µg/L were also detected. In the summer months, diclofenac concentration in the Neue Luppe exceeded 5 µg/L (Fig. 8, top). In the WWTP effluents and the receiving water bodies, there is a diclofenac peak in the summer months. This peak is not found at the sites Mulde and Luppa, where the concentrations fluctuate more randomly (Fig. 8, bottom).

Ternes (1998) measured diclofenac concentrations in German streams and waste water treatment plants in 1996 [46]. The maximum concentration detected during that time was 1.2 µg/L in the streams and 2.1 µg/L in the waste water treatment plants. Comparison of these data with our results from 2020 implies that the diclofenac concentrations in German surface waters increased over the last 25 years. An increase was also detected in the Saxon Drug Report, where the concentration in the river Mulde increased successively between 2008 and 2010 from below 50 ng/L to more than 100 ng/L [47]. In the present study, the diclofenac concentrations in the Mulde range from 100 ng/L to 200 ng/L. Therefore, our results confirm the previously noted increase in diclofenac concentrations, and actually suggest this increase has continued further until (at least) 2020.

The predicted no effect concentration (PNEC) of diclofenac derived by the European Union is 0.05 µg/L [48]. At 21 of 24 measuring sites for the EU watchlist in Germany, the PNEC was exceeded, at other national sites exceedances could be measured at 75 % of the sampling sites [45]. In this study, only the reference site Altenhainer Bach and the small stream Luppa remained below this threshold. However, it should be noted that the peak diclofenac concentrations at the site Luppa are within the threshold respecting the uncertainty margin (Fig. 8, bottom). Therefore, it is likely that adverse effects for aquatic organisms occur, though the concentrations are reduced up to a factor of 1000 in the receiving waters compared to the WWTP effluents.

While the concentrations of diclofenac fluctuated during the sampling campaign, the concentrations of benzotriazole remained fairly constant (Fig. 8). Benzotriazole is used as a corrosion inhibitor for dishwashers, copper, or in de-frosting salts [49]. The compound is commonly detected in European surface waters and WWTP effluents [29,48]. Highest concentrations were detected in the WWTP effluents in concentrations between 1 µg/L to 15 µg/L. At the WWTP in Leipzig, TWA concentrations were always above 5 µg/L. TWA concentrations in the WWTP effluents are in line with the mean concentration of benzotriazole detected by Loos et al. (2013) in European WWTP effluents (6.3 µg/L) [29]. In the streams, concentrations above 1 µg/L were frequently detected in the receiving water courses of the WWTPs. At the site Luppa, concentrations of benzotriazole were generally below 10 ng/L, with one exception in October
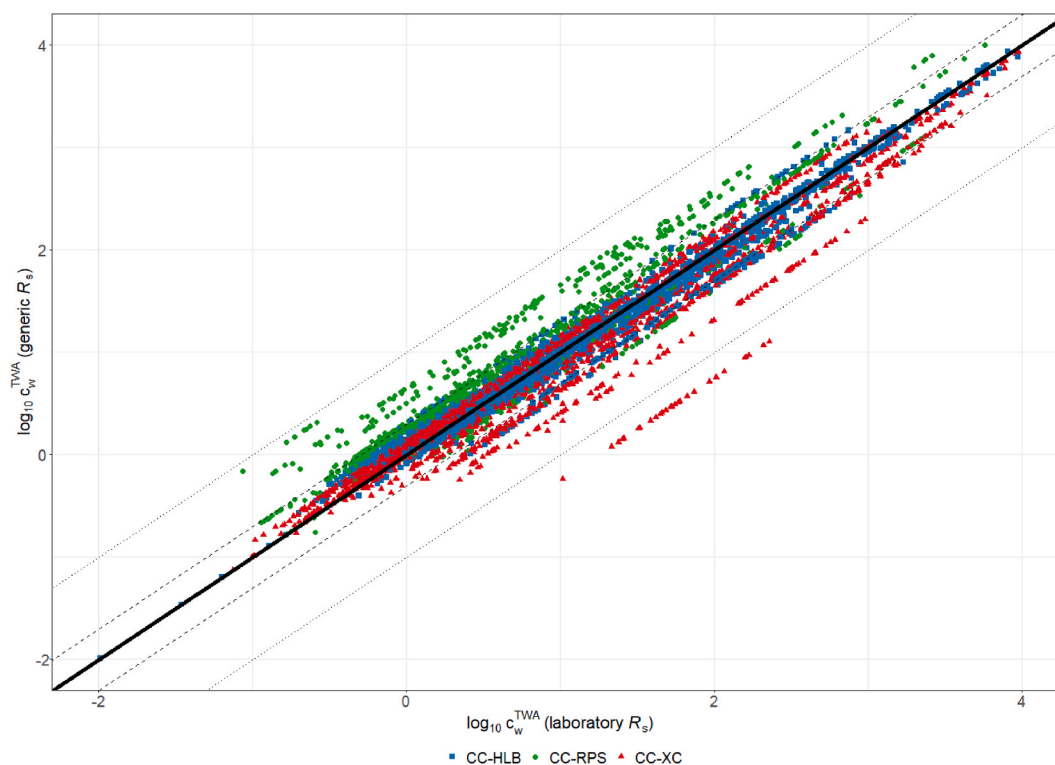
Fig. 9. Comparison of TWA concentrations derived using individual sampling rates (x-axis) and generic sampling rates (y-axis), respectively. Individual sampling rates were taken from Römerscheid et al. (2023) [28].

2020. At the reference site, benzotriazole was detected in concentrations between 1 ng/L to 7 ng/L which is similar to the concentrations at the site Luppa. This shows that the anthropogenic input on the different sampling sites decreases from strongly influenced WWTPs and receiving water bodies to less impacted small streams. In European streams, a mean benzotriazole concentration of 493 ng/L was detected [48]. The higher concentrations in this study may be attributed to the selection of sampling sites with higher urban impact than in the study across Europe, which also included very pristine sites.

The antiepileptic drug carbamazepine is prescribed for a variety of psychological conditions. The PNEC is 2 μg/L in surface waters [50]. This concentration was not exceeded in this study, however the concentration in the WWTPs Grimma and Leipzig commonly can be found above 1 μg/L. In an EU-wide survey, a mean concentration of 248 ng/L could be detected [48], which is similar to concentrations of the compound at the site Neue Luppe (Fig. 8). Carbamazepine is on the national watchlist, but does not generally exceed the EQS of 500 ng/L in the national monitoring [45]. This is in good agreement with results of this study. Concentrations detected in WWTPs in the Saxon Drugs Report 2011 are generally larger than concentrations detected in WWTPs in this study. This implies that there might have been a reduction of prescription [47].

3.4. Application of generic sampling rates in field sampling

This study shows the advantages and limitations of generic sampling rates and their application in field sampling. Generic sampling rates give the option to estimate TWA concentrations for compounds with known and unknown uptake kinetics. In Fig. 9 we plotted all TWA concentrations calculated with generic R_s against those determined using the specific R_s values (as far as available). Most TWA-concentrations are comparable within a factor of 2 (dashed lines). CC-RPS tends to overestimate TWA-concentrations when using generic sampling rates, but values are still within a factor of 10 (dotted lines). Only clotrimazole determination in CC-XC is below the 1:10 line in Fig. 9. That is because the uptake rate of this relatively nonpolar compound (log K_{ow} = 6.3) is very low (0.007 L/d) compared to the generic sampling rate. This suggests that one limitation of the use of generic sampling rates are nonpolar compounds. However, generally Chemcatchers are applied for compounds with log K_{ow} < 4.0. Fig. 9 additionally shows that general comparability between passive samplers is given and the error is systematic due to the application of the generic sampling rates. This confirms that an application of generic R_s for transformation products or compounds without calibration data is acceptable to yield a raw estimate of environmental concentrations.

However, TWA concentrations are relatively uncertain, which also shows in the error bars in Figs. 5–8. Therefore, if specific calibration data are available they should always be the first choice to yield more precise TWA concentrations.

4. Conclusions

Through employing generic sampling rates, certain Chemcatcher passive samplers (PS) yield comparable TWA concentrations for polar organic compounds. In this way, passive sampling provides practically useful information about solutes of potentially high concern even at very low concentrations, and as such may support regulatory monitoring. To this end, CC-RPS and CC-XC tend to be more sensitive for concentrations below 10 ng/L as compared to CC-HLB. By contrast, thermodynamic equilibrium PDMS are less suited for polar xenobiotics such as respective pesticides, pharmaceuticals and their transformation products (TPs).

Regarding bioactive agents and their TPs, PS analysis enables to discriminate agricultural from urban use patterns (pesticides vs pharmaceuticals) as well as recent from earlier applications (ratio of parent compound vs TP), and may also unravel illegal use of already banned xenobiotics (e.g. atrazine) that could support their actual elimination from hidden applications. For the WWTPs and surface waters in the Saxon Leipzig-Grimma region, compliance with RAC and EQS thresholds in most cases indicates a relatively good chemical status except for the neonicotinoid imidacloprid (EU-banned), the inflammatory drug diclofenac (frequently exceeding its PNEC), and atrazine (banned long ago). Overall, the results demonstrate the PS application for identifying low-concentration xenobiotics of high concern that are difficult to detect through conventional grab sampling. Despite systematic deviations, it could be shown that a conservative estimation of environmental concentrations is possible with generic sampling rates in field studies. This broadens the applicability of passive samplers for different water bodies, miropollutants and sampler types.

CRediT authorship contribution statement

Mara Römerscheid: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Albrecht Paschke:** Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Gerrit Schüürmann:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e23378.

ABBREVIATIONS

CC	Chemcatcher
ATZ	atrazine
CC-HLB	Chemcatcher equipped with Atlantic HLB-L disk
CC-RPS	Chemcatcher equipped with Attract SDB-RPSdisk
CC-XC	Chemcatcher equipped with Attract SDB-XC disk
CDZ	chloridazon, DAR: deethylatrazine-atrazine-ratio
DP-CDZ	dephenyl chloridazon
EQS	environmental quality standard
HLB	hydrophilic lipophilic balance
MTL	metolachlor
MTZ-ESA	metazachlor 2-oxoethanesulfonic acid
MTZ-OA	metazachlor oxanilic acid
PDMS	polydimethylsiloxane
PNEC	predicted no-effect concentration
RAC	regulatory acceptable concentration
SDB-RPS	styrene divinyl benzene reversed phase sulfonate
SDB-XC	styrene divinyl benzene (exchange)

TBZ   terbuthylazine
TP   transformation product
TWA   time-weighted average
WWTP waste water treatment plant

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