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Calibration and Field Application of the Atlantic HLB Disk Containing Chemcatcher® Passive Sampler – Quantitative Monitoring of Herbicides, Other Pesticides and Transformation Products in German Streams

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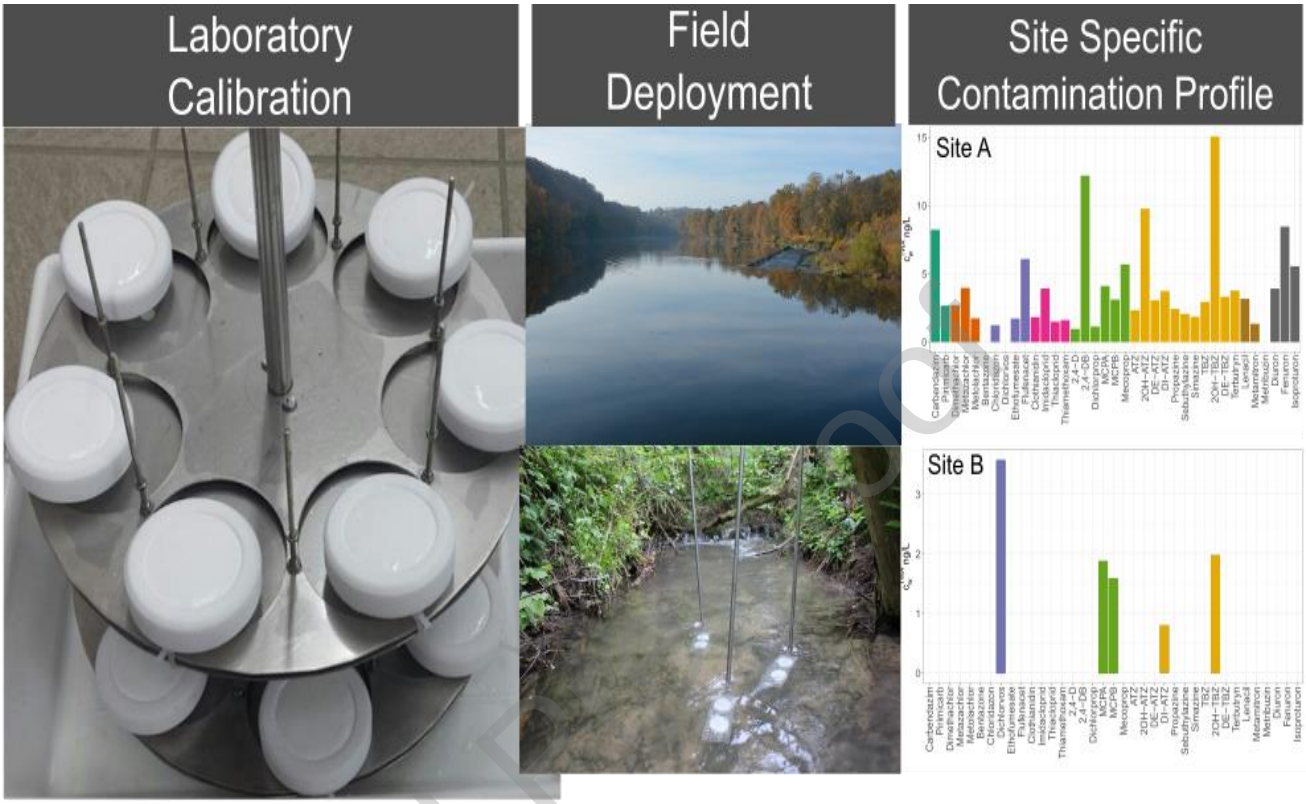
KEYWORDS Passive Sampling, Water Monitoring, Atlantic Disk, Polar Pesticides, Transformation Products

ABSTRACT. The Chemcatcher® (CC) passive sampler containing an Atlantic HLB-L Disk (AD) was calibrated in a laboratory-based flow-through tank over 21 days under stirring for 38 polar organic pesticides with log K_{ow} ranging from -1.7 to 3.8. The resultant sampling rates R_s range from 0.025 to 0.068 L/d. In 2018, field trials were conducted in the German rivers Mulde and Havel, as well as in 7 agricultural streams in Lower Saxony and Saxony-Anhalt. For 36 detected pesticides, the overall low concentrations were 0.2 – 49.4 ng/L. The determined pesticide profiles reflect agricultural use and were dominated by triazine herbicides including transformation products, by neonicotinoid insecticides, and by the herbicide mecoprop. Additional single hot spots were provided by the herbicides metamitron, isoproturon, and MCPA (showing the overall largest value of 49.4 ng/L). Notably, the detected waterborne pesticides include banned herbicides and associated transformation products in concentration ratios suggesting also recent input. This concerns in particular atrazine and its transformation products 2-OH-atrazine, deethylatrazine and deisopropylatrazine. An extended target screening of AD-CC extracts in the river Havel revealed the additional presence of other organic micropollutants including biocides, surfactants and industrial chemicals, and demonstrated the AD-CC applicability up to log K_{ow} of 4.5.

GRAPHICAL ABSTRACT



1. Introduction

Modern agriculture relies on the use of plant protection agents that are often termed pesticides, covering also herbicides, fungicides and other bioactive agents besides insecticides. However, excessive pesticide use significantly contributes to non-target toxicity in freshwater ecosystems.[1, 2] Especially small water bodies in rural areas may be substantially affected by field run-off from agriculture.[3] Chemical monitoring is necessary to assess the anthropogenic impact on aquatic communities, which is recognized by the legislative authorities in many countries. In the European Union the Water Framework Directive (WFD) aims to increase biological and chemical water quality by focusing on selected priority pollutants. While this list includes pesticides, pharmaceuticals and industrial compounds of great concern,[4] it is still incomplete. However, due to different analytical and monitoring strategies prioritization of future candidates is difficult.[5]

The human exposome is considerably influenced by chemicals in the environment, too. As pointed out by the Lancet Commission on Pollution and Health, 16% of premature deaths worldwide can be linked to pollution.[6] A key element to understanding the exposome and the eco-exposome is chemical analysis. If the latter is applied in the right time and place, adverse outcome pathways may directly be linked to the uptake of bioactive compounds from the environment. The exposure of short-lived aquatic organisms for example is best quantified using time-integrated monitoring approaches because these methods include short-term peaks, which may carry considerable pollution loads.[7]

Besides monitoring, modelling can increase knowledge of material flows and environmental sinks and fill information gaps arising from the limits of discrete sampling. However, exposure and fate predictions rely on high quality input data.[8] It is increasingly accepted in the scientific community that periodic (monthly or weekly taken) spot samples are not suitable to quantify the average exposure of aquatic organisms to waterborne contaminants, especially regarding pulsed or otherwise fluctuating pesticide concentrations in smaller agricultural streams.[9, 10] In particular, snapshot sampling does not inform about background (long-term) exposure levels. Moreover, grab sampling requires an additional clean-up to discriminate the dissolved fraction – often considered as bioavailable – from the portion bound to colloidal organic matter.

Time-integrative sampling techniques can overcome these monitoring deficiencies. Composite sampling is one option but requires expensive technical equipment, infrastructural requirements and mostly personnel on site. Traditional bottle sampling needs to be done at least daily for obtaining representative results, which increases the costs for collection, transportation, processing and analysis of samples considerably. Passive samplers offer several advantages for continuous monitoring of aqueous micropollutants over discrete periodic water sampling, especially in rural areas. Analytes are accumulated over a deployment time of days to weeks in the receiving sampling phase, and therefore provide low detection limits. Furthermore only the (truly) dissolved and hence biologically available fraction of contaminants is sampled.[11]

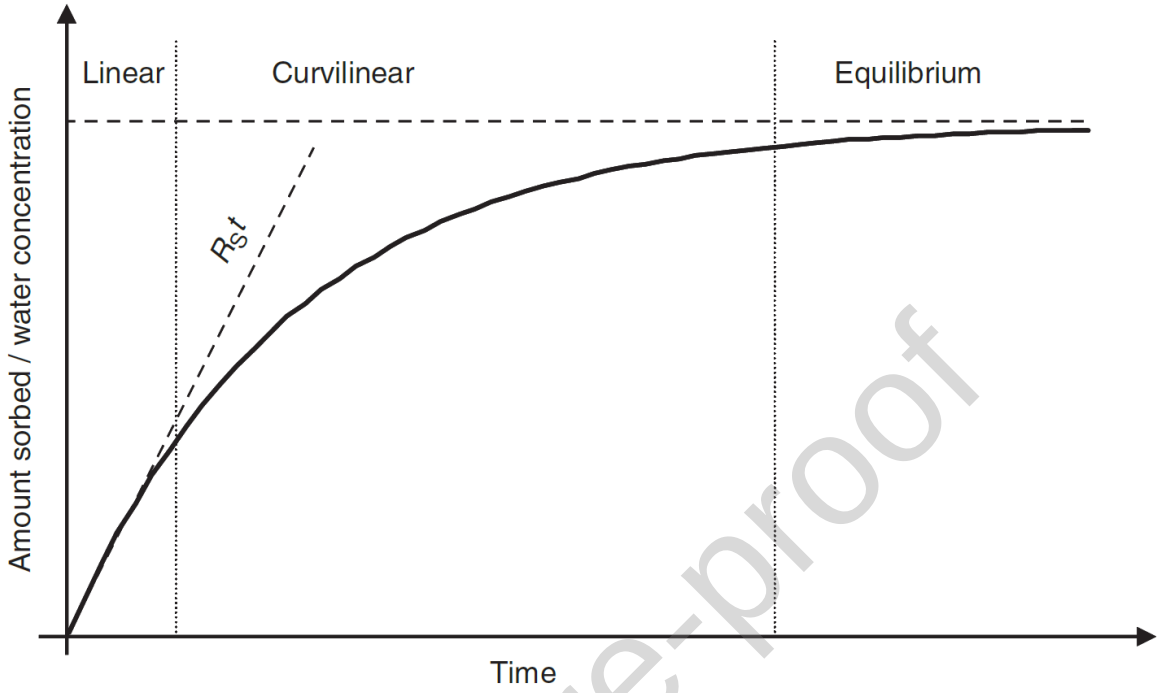


Figure 1: Uptake of analytes in passive samplers, taken from Schulze *et al.*[12] with permission by the authors.

Passive samplers may be designed such that their accumulation of waterborne contaminants is similar to their bioconcentration (without metabolism) in biota, following first-order mass transfer kinetics.[13] Due to successive saturation of the sampler, there are different periods (modes) of sampling (**Figure 1**). During the initial linear uptake period, analyte desorption from the sampler can be neglected (integrative sampling mode). As the desorption rate increases, the uptake curve flattens and finally thermodynamic equilibrium is reached. The device acts now as a so-called equilibrium sampler. Generally with inclusion of the aforementioned limiting cases, the uptake into the sampler can be fitted using equation (1). [14]

$$c_s(t) = c_w \cdot \frac{k_1}{k_2} \cdot [1 - \exp(-k_2 \cdot t)] \quad (1)$$

Where k_1, k_2, c_s and c_w denote the uptake and elimination rate constants as well as the compound concentrations in the sampler and in water, respectively. Note that equation (1) assumes c_w to be constant during the sampling period.

Equilibrium sampling enables the determination of c_w, provided the sampler-water partition coefficient K_{sw} is known. Dependent on the uptake/elimination kinetics, however, the thermodynamic equilibrium will follow concentration fluctuations. The latter may range from delayed adaption to approximating a snapshot of the situation during sampler retrieval. Integrative sampling periods typically last between several days to weeks, and thus result in time-weighted average (TWA) c_w values. During the integrative sampling phase equation (1) can be reduced to equation (2), with R_s denoting the sampling rate during the period of time t, and m_s representing the mass of the sampled compound.[14] For more details on the theoretical principles of passive samplers and on general guidance for their calibration and application we refer esp. to Greenwood *et al.* (2007)[15] and the international standard ISO 5667-23:2011 on passive sampling in surface waters.

$$m_s = R_s \cdot t \cdot c_w \quad (2)$$

A variety of passive samplers has been designed to accumulate water contaminants from various chemical classes, covering polar and nonpolar organics as well as organometallics and inorganics (e.g. phosphate, nitrate and metal ions).[10] Specifically for polar and semipolar pesticides with logarithmic octanol-water partition coefficients (log K_{ow}) below 4, the following two sampler types are commercially available: The polar organic chemical integrative sampler (POCIS) introduced by Alvarez and co-workers

from U.S. Geological Survey[16], and the Chemcatcher® (CC) developed by Greenwood and Mills at the University of Portsmouth, U.K.[17]

The POCIS consists of a sorbent powder enclosed between two microporous filter membranes. It was tested in an inter-laboratory study organized in 2011 by the NORMAN association (Network of reference laboratories for monitoring emerging environmental pollutants) together with the European DG Joint Research Centre[18] for selected pesticides among other target compounds, and found afterwards several applications in larger pesticide monitoring campaigns (e.g. Ahrens *et al.*, 2015[19]). A practical disadvantage of this tool is the often occurring substantial displacement and/or loss of sorbent material during field deployment and subsequent processing in the laboratory. In particular, comparison of the Chemcatcher and POCIS performance for detecting pharmaceuticals unraveled an inhomogenous distribution of sorbent material within POCIS that may impair the accuracy of uptake calibration (sampling rates) and the resultant monitoring data (TWA concentrations).[20]

The Chemcatcher has the general advantage that the receiving phase for the accumulation of contaminants is bound to an inert polymeric disk matrix, which prevents leakage during field exposure and loss of material during processing. Mostly used with a protective (and diffusion-limiting) membrane covering the sorbent disk, the Chemcatcher has been calibrated and applied for the time-integrative monitoring of plant protecting agents in water.[21–23] Respective polar pesticides include triazines and phenylureas (herbicides) as well as neonicotinoids and carbamates (insecticides). Specific Empore Disks manufactured by the company 3M were used in nearly all pesticide-related Chemcatcher applications published so far, namely the

poly(styrenedivinylbenzene) copolymers SDB-XC and SDB-RPS, respectively. Microporous polyethersulfone (PES) filter plates of pore size 0.2 µm or 0.45 µm were mostly used as protective membranes.

In 2018, 3M stopped the production of the widely used Empore Disk. To both overcome a shortage of material and to extend the range of passive samplers suitable for the quantitative monitoring of polar pesticides, the exploration and calibration of alternative devices is of interest. A relatively new disk format, marketed by Biotage, the Atlantic HLB-L Disk (AD), is using a hydrophilic-lipophilic balanced sorbent (HLB) as a receiving material and may overcome several disadvantages of the POCIS. The material is fixed in a glass fibre filter, which prevents loss during deployment and sampler disassembly. Furthermore the disk can be used in the Chemcatcher housing. Previous Atlantic HLB-L disk applications concern the quantification of pharmaceuticals in waste water employing an in situ calibration[24], and of metaldehyde in the UK.[25] To the best of our knowledge, however, there has been no study so far providing sampling rates R_s for quantifying commonly used pesticides in the field.

Thus, the goal of the present study was to calibrate the Atlantic disk HLB-L as Chemcatcher sampling phase (AD-CC) for quantifying polar pesticides in surface waters, and to apply the accordingly derived sampling rates R_s for evaluating the pesticide profile of German streams and rivers in 2018. To this end, organic herbicides and other pesticides including some transformation products were selected with log K_{ow} ranging from –1.7 to 3.8. A further objective was to explore the AD-CC suitability for an extended target screening in the field employing HPLC-HRMS as a potentially additional AD-CC application area.

2. Material and Methods

2.1. Chemicals

33 Pesticides (26 herbicides, 6 insecticides and the fungicide carbendazim, covering 11 different substance classes) as well as 5 abiotic and biotic herbicide transformation products were purchased from HPC Standards (Cunnersdorf, Germany) as solids with analytical purity (Table SM-1). Internal standards (Mecoprop-d3 and Imidacloprid-d4) were bought from HPC Standards as solutions (c = 100 µg/mL). Water was bidistilled prior to use. Methanol and acetonitrile were purchased from VWR in HPLC-grade. PES membranes (0.45 µm) were obtained from Pall. Atlantic HLB-L Disks were purchased from Horizon Technologies. Chemcatchers® (d = 47 mm) were ordered from AT Engineering Technology, Tadley/UK.

2.2. Sampler Preparation

PES membranes were rinsed with methanol and water for 30 min each. Until assembly of the Chemcatchers, the membranes were submerged in water. Atlantic disks were prepared by elution with 50 mL of methanol and 50 mL of water. Subsequently, the disks were dried by applying a gentle vacuum to them. Prepared disks were placed in clean and dry Chemcatcher bodies and covered with a conditioned PES membrane. Water was pipetted on the membrane to keep the disk wetted until deployment. The Chemcatchers were stored up to 24 h at 4°C before placing them in water.

2.3. Calibration Experiment

The calibration experiment was conducted in a 30 L stainless steel tank. 14 samplers were placed on a two-storied carrousel and replaced by new samplers successively in duplicates (one from the top, one from the bottom shelf) to cover a time range of 2 to 21 days of exposure with 14 data points. The replacement schedule can be found in Table SM-2. Temperature was kept at a constant level by placing the apparatus in a climate chamber (Figure SM-1). An electric stirrer (Heidolph, Germany) was run at 40 rpm to simulate a water flow of approximately 40 cm/s, which can be found in small streams. Tap water was pumped at a rate of 5 L/h using a pump (Prominent Gamma/4). The pesticide solution was added continuously at a flow rate of 5 mL/h using a peristaltic pump (Gilson, Minipuls 3). Before starting the calibration of the samplers, the tank (walls, carousel) and tubings were left to pre-saturate for several days. Temperature, pH and water concentrations were monitored daily during the experiments. Though the spiking solution was added at the top of the tank, concentrations in AD-CC are generally similar in samplers from the upper and lower shelf of the carrousel as confirmed by the statistical (non-systematic) within-duplicate scatter. This indicates that the spiking solution is distributed evenly within the tank by the stirrer.

2.4. Extraction of Samplers

2.4.1. Passive Samplers

Samplers from the laboratory experiment were disassembled and extracted immediately after retrieval. Before extraction, the disks were dried for approximately five minutes using a gentle vaccum to remove the water within the glass fibre filter. The

disks were extracted with 40 mL methanol by elution and reduced to 1 mL using a Turbovap II (Zymark) at a water temperature of 35°C. Samples from the calibration experiment up to day 10 were further concentrated to a final volume of 0.5 mL. 10 µL (c = 10 µg/mL) of internal standard were added to each sample after evaporation. Samples were stored at 4°C until analysis.

2.4.2. Water Samples

During the calibration experiment compound concentrations in water were monitored regularly using solid phase extraction (SPE). SPE cartridges (Macherey Nagel Chromabond HLB, 6 mL/500 mg) were conditioned with 10 mL methanol and 10 mL bidistilled water. Subsequently, 1 L of water was run over the cartridge. The cartridge was left to dry for 30 min and eluted using 10 mL methanol and 10 mL acetonitrile. The extracts were evaporated under a nitrogen stream to 1 mL using a Turbovap II (Zymark). 10 µL (c = 10 µg/mL) of internal standard were added to each sample after evaporation. Samples were stored at 4°C until analysis.

2.5. Field Study

In June 2018, duplicate samplers were deployed in seven small streams in the German federal states Lower Saxony and Saxony-Anhalt for 18 to 22 days. Six of these sampling sites were located in rural areas with at least 60% of agriculture (stream 1: only 36%). The seventh site served as reference site, located in a forest without agricultural impact. The Chemcatchers were placed on meshes shortly above the sediment (Fig SM-2a and SM-2b). In November 2018, duplicate samplers were placed in the river Mulde downstream the sewage treatment plant of the city Grimma (Saxony,

Germany) for 21 days in a cage. Furthermore, samplers were deployed in the river Havel in the city Potsdam (German state Brandenburg) in two successive periods in July and August of 2018 in triplicates for 28 days. In this site, cages equipped with Chemcatchers were hung to a buoy (Figure SM-3a and SM-3b) in 1 m depth. A map of the sites can be found in **Figure 2**. After exposure, samplers were stored at 4°C for up to 24 h before disassembly and extraction. Trip blanks were used to monitor background contamination during sampler preparation, transport to and from the sampling sites, and extraction. During the deployment of the field samplers, the blanks were stored at 4°C in the laboratory. Throughout HPLC analysis, method blanks were used to detect carry over effects and background concentrations of the analytical method. All samplers exposed were extracted and analyzed separately using HPLC-MS/MS. Time-weighted-average (TWA) water concentrations $c_{\mathrm{w}}^{\mathrm{TWA}}$ were calculated from the laboratory-calibrated sampling rates R_{s} [L/d] and the pesticide masses m_{s} [ng] found in the samplers after exposure time t [d], using the formula for the time-integrating sampling period[15] (3):

$$c_{\mathrm{w}}^{\mathrm{TWA}} = \frac{m_{\mathrm{s}}}{R_{\mathrm{s}} \cdot t} \qquad \textbf{(3)}$$

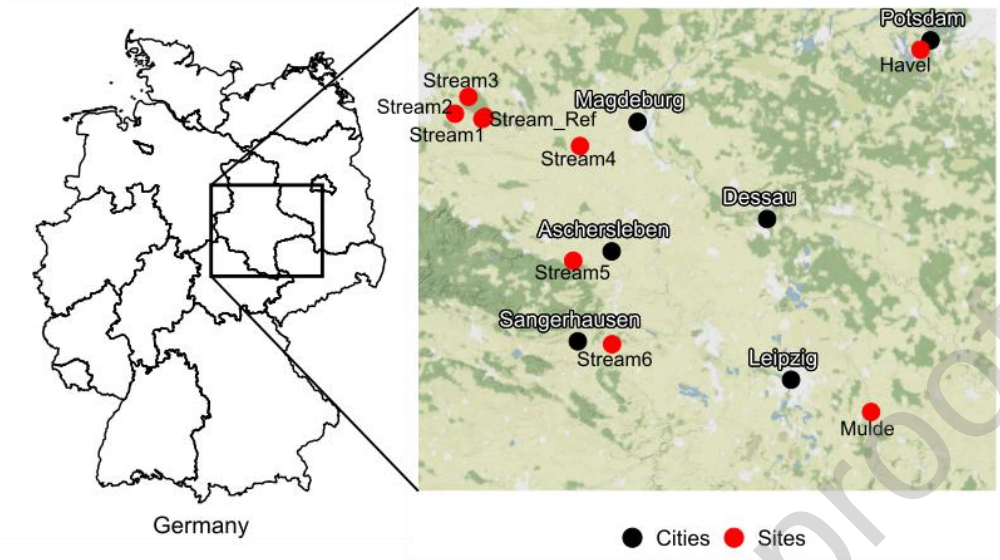


Figure 2: Sampling sites monitored in field campaign.

2.6. Target Analysis

Samples were analysed using a 1290 Infinity series HPLC coupled with a 6460 TripleQuad mass spectrometer (Agilent Technologies). The HPLC was equipped with a Kinetex EVO C18-column (2.6 µm particle size, 50 mm x 3 mm) with a guard column (Phenomenex). Bidistilled water with 0.1% formic acid was used as eluent A. Acetonitrile with 0.1% formic acid was used as eluent B in the positive mode, and acetonitrile without additives as eluent B in negative mode. In positive ionization mode the gradient started at 5% B. B was raised to 10% within 2 min. The gradient was increased to 35% in the next 8 min, followed by a further increase to 60% within additional 4 min. The total runtime was 14.5 min. In the negative ionization mode, the gradient started at 10% B and was increased to 30% in the first min. It was raised

further to 55% within the next 5 min, leading to a total runtime of 6 min. After each run the column was flushed by increasing B to 100% and holding that for 1 min. Subsequently, the gradient was returned to the initial composition, and the column was left to equilibrate for 1 min. Two mass transitions were analysed in dynamic MRM mode as far as possible (Table SM-1). Limits of detection (LOD) and of quantification (LOQ) can be found in Table SM-3.

2.7. Extended target screening

Field extracts from the river Havel were screened additionally for a larger set of 677 compounds commonly occurring in surface waters using a Thermo Ultimate 3000 LC system coupled to a quadrupole-Orbitrap instrument (Thermo QExactive Plus) with electrospray ionisation. 70 µL of passive sampler extracts were diluted with 30 µL bidistilled water prior to the measurement. For the LC separation we used a Kinetex EVO C18-column (50 mm × 2.1 mm, 2.6 µm particle size, Phenomenex, pre-column 4 mm x 2.1 mm and in-line filter 0.2 µm) with a gradient elution consisting of water with 0.1% of formic acid and methanol containing 0.1% of formic acid at a flow rate of 300 µL/min. After 1 min of 5% B, the fraction of B was linearly increased to 100% within 12 min and 100% B were kept for 11 min. The eluent flow was diverted to waste and the column was rinsed for 2 min using a mixture of isopropanol + acetone50:50/eluent B/eluent A (85%/10%/5%) to elute hydrophobic matrix constituents for cleaning. Subsequently, the column was re-equilibrated to initial conditions for 5.7 min. The injection volume was 5 µL and the column was operated at 40°C. Separate runs were conducted in positive and negative ion mode combining a full scan experiment (100-1500 m/z) at a nominal resolving power of 70,000 (referenced to m/z 200) and data-

independent MS/MS experiments at a nominal resolving power of 35,000 with twelve different isolation windows. For the latter, we acquired the data using broad isolation windows of about 50 mu (i.e., m/z ranges 97-147, 144-194, 191-241, 238-288, 285-335, 332-382, 379-429, 426-476) and 260 mu (i.e., m/z ranges 473-733, 729-989, 985-1245, 1241-1501), respectively.

Peak detection was done with MZmine 2.3 [26] after conversion of the raw data files to mzML format of ProteoWizard[27] using the following processing steps: (i) Mass detection, (ii) ADAP chromatogram builder [28], (iii) smoothing, (iv) Chromatogram deconvolution, (v) alignment of peak lists, and (vi) gap filling. Target compounds were finally annotated based on retention time and accurate mass by custom library search, and the annotated peak list was exported as a csv file. Diagnostic MS/MS product ions were used for confirmation of the detected compounds in ambiguous cases. MZmine settings can be found in Table SM-4.

Peak heights were compared to trip blanks and method blanks and those below the blank values were removed from the dataset. Out of 48104 peaks found in positive and negative mode, 290 compounds could be identified based on retention time and accurate mass in the field samples. Only identified peaks were considered for data evaluation. Mean concentrations of triplicates were calculated, and only compounds found in all triplicates were considered for further data evaluation. Concentrations were estimated using a one-point-calibration of 100 ng/mL for concentrations below 300 ng/mL. Higher concentrations were estimated using a 1000 ng/mL standard. Since no sampling rates were available for most compounds, only masses (ng/disk) were used for comparison.

3. Results and Discussion

3.1. Calibration Experiments

The new Chemcatcher version was calibrated in the laboratory for 21 days. The average water temperature was 14.8°C during the experiment. The experiment was conducted in a temperature-controlled environment. Average compound concentrations in water ranged from 9 ng/L to 33 ng/L during the calibration experiment, with 2-hydroxyatrazine being an outlier with an average concentration of 86 ng/L. It could be found in the tap water in low concentrations (10 ng/L) and was also monitored in the experiments. Atrazine (ATZ) hydrolysis to its 2-hydroxy transformation product 2-OH-ATZ occurs abiotically and as metabolic conversion,[29–31] and the high background concentrations of 2-OH-ATZ reflect its significantly lower readiness to further abiotic degradation. Possibly, ATZ hydrolysis took also place in the stock solution, raising further the concentration of 2-OH-ATZ.

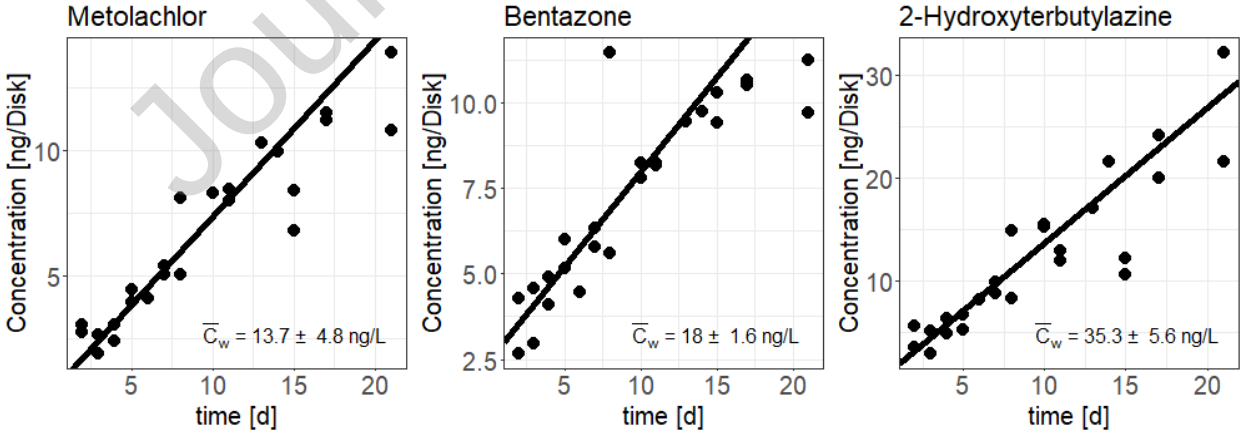


Figure 3: Pesticide uptake curves obtained from the calibration experiment. Most compounds stay within the linear uptake phase for three weeks.

Table 1: Sampling rates R_s of the Atlantic Disk Chemcatcher for 38 pesticides including 5 transformation products covering 26 herbicides, 6 insecticides and 1 fungicide. Rows marked in grey indicate compounds that were compared to literature data[21] in **Figure 4**.

	Compound	Application	log K_{ow} [a]	f_{ionic} [b]	R_s (L/d)	s(R_s) [c] (L/d)
Carbamate						
1	Carbendazim	Fungicide	1.55 (1.55)	<0.01	**0.025**	0.005
2	Pirimicarb	Insecticide	1.4		**0.040**	0.005
Chloroacetanilide						
3	Dimethachlor	Herbicide	2.33		**0.039**	0.006
4	Metazachlor	Herbicide	2.38		**0.037**	0.005
5	Metolachlor	Herbicide	3.24		**0.049**	0.017
Miscellaneous						
6	Bentazone	Herbicide	1.67 (-3.05)	1	**0.030**	0.004
7	Chloridazon	Herbicide	0.76		**0.068**	0.011
8	Dichlorvos	Insecticide	0.6		**0.056**	0.010
9	Ethofumesate	Herbicide	2.89		**0.059**	0.020
10	Flufenacet	Herbicide	2.39		**0.035**	0.005
11	Quinmerac	Herbicide	2.87 (-7.97)	1	**0.057**	0.014
Neonicotinoids						
12	Clothianidin	Insecticide	0.64 (0.64)	<0.01	**0.046**	0.007
13	Imidacloprid	Insecticide	-0.41 (-0.43)	0.039	**0.053**	0.007
14	Thiacloprid	Insecticide	2.33		**0.065**	0.009
15	Thiamethoxam	Insecticide	0.8		**0.053**	0.009
Phenoxyacetic acid derivatives						
16	2,4-D	Herbicide	2.62 (-2.40)	1	**0.046**	0.013
17	2,4-DB	Herbicide	3.60 (0.16)	1	**0.030**	0.006
18	Dichlorprop	Herbicide	3.03 (-1.94)	1	**0.028**	0.004
19	MCPA	Herbicide	2.52 (-2.34)	1	**0.040**	0.005
20	MCPB	Herbicide	3.50 (0.08)	1	**0.036**	0.005
21	Mecoprop	Herbicide	2.94 (-1.87)	1	**0.025**	0.003
Triazines						
22	Atrazine	Herbicide	2.82		**0.053**	0.007
23	2-Hydroxyatrazine	Metabolite	-1.74 (-2.23)	0.676	**0.029**	0.005
24	Deethylatrazine	Metabolite	1.78		**0.055**	0.008
25	Deisopropylatrazine	Metabolite	1.36		**0.044**	0.006
26	Propazine	Herbicide	3.24		**0.050**	0.006
27	Sebuthylazine	Herbicide	3.31		**0.051**	0.006
28	Simazine	Herbicide	2.4		**0.052**	0.007
29	Terbutylazine	Herbicide	3.27		**0.048**	0.006
30	Deethylterbutylazine	Metabolite	2.23		**0.061**	0.009
31	2-Hydroxyterbutylazine	Metabolite	-1.29 (-1.75)	0.651	**0.029**	0.005
32	Terbutryn	Herbicide	3.77		**0.046**	0.006
Triazinones						
33	Lenacil	Herbicide	2.23 (2.23)	<0.01	**0.049**	0.006
34	Metamitron	Herbicide	1.44		**0.049**	0.006
35	Metribuzin	Herbicide	1.49		**0.057**	0.007
Phenylureas						
36	Diuron	Herbicide	2.67 (2.67)	<0.01	**0.033**	0.004
37	Fenuron	Herbicide	1.38 (1.38)	<0.01	**0.044**	0.005
38	Isoproturon	Herbicide	2.84 (2.84)	<0.01	**0.035**	0.004

[a] log K_{ow} from KOWWIN (Episuite).[32] Parentheses contain the ionization-corrected octanol-water partition coefficient D_{ow} at pH = 8 calculated through $D_{ow} = K_{ow} \cdot \frac{1}{1+10^{(pH-pK_a)}}$ with pK_a from ACD Labs[33].

[b] Ionic fraction calculated from the Henderson-Hasselbalch-equation at pH = 8: $f_{ionic} = 1 - \frac{1}{1+10^{(pH-pK_a)}}$

[c] Standard error *s* of R_s calculated with Gaussian error propagation: $s(R_s) = \sqrt{\frac{s(c_w)}{c_w} + \frac{s(a)^2}{a^2}} \cdot R_s$, with slope *a* of the linear uptake phase, and waterborne compound concentration c_w.

Sampling rates were calculated from uptake curves using all data points within the linear uptake phase. AD-CC showed a linear uptake phase over three weeks for all compounds except for two: Bentazone left the linear uptake phase after day 15, and quinmerac uptake became nonlinear after 7 d (**Figure 3**, Fig SM-37). Accordingly, for bentazone and quinmerac only the data points from day 2 to day 15 and from day 2 to day 7, respectively, were used for deriving R_s values.

Calculated sampling rates range from 0.025 to 0.068 L/d (**Table 1**). For comparison, twelve sampling rates of the Chemcatcher containing an Empore Disk SDB-RPS as receiving phase (ED-CC) were taken from Vermeirssen *et al.* (2012)[21] (compounds of rows marked in grey in **Table 1**), who conducted a calibration experiment in a flow-through channel system. The data are plotted in **Figure 4**. Six compounds are close to the 1:1-line and can be fitted linearly with the equation R_s(AD-CC) = 0.7904 • R_s(ED-CC)[21] + 0.0062 (R^2 = 0.949, n = 6). These compounds cover different compound classes, but have in common a logarithmic ionization-corrected octanol-water partition distribution coefficient (log D_{ow}) at pH = 8 below 2.7. Note, however, that carbendazim with log D_{ow} = 1.55 is an outlier to this relationship. As can be seen from Figure 4, for six compounds R_s(AD-CC) is below R_s(ED-CC) by factors of 2-3, indicating correspondingly lower sensitivities of AD-CC as compared to ED-CC.

As discussed in other studies, uptake kinetics may be affected by molecular properties and structural features such as molecular size, atomic composition, structural connectivity, chemical bonding features, and non-covalent intermolecular forces.[34, 35] Taking these considerations into account, a presently ongoing study is devoted to investigating the AD-CC vs ED-CC relationship for additional compounds, and to

explore further options for relating R_S differences to physicochemical and molecular properties of the compounds.

Whereas AD-CC tends to yield lower R_S values than ED-CC, its linear uptake phase of 3 weeks compares favorably to ED-CC with only 2 weeks, enabling a correspondingly longer exposure time (Preliminary results of unpublished experiments even suggest linear uptake for four weeks and more). Accordingly, AD-CC is better suited for settings in combination with (sufficiently fast) equilibrium samplers, thus providing information about both uptake kinetics and biomimetically simulated bioconcentration.

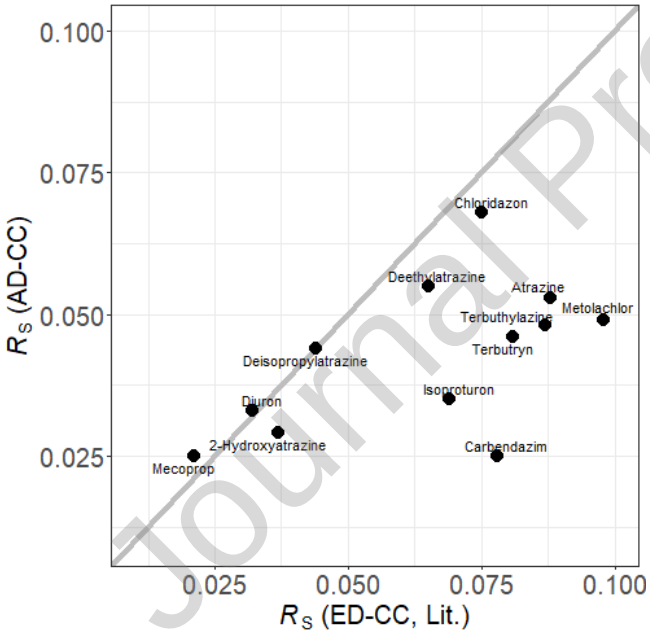


Figure 4: Comparison of sampling rates R_S in ED and AD. The line shows the 1:1-relation between the samplers for the 12 compounds (# 1, 5, 7, 21-25, 29, 32, 36, 38 in Table 1) with ED-CC data available from literature.

3.2. Field study

At the sampling sites, the flow rates ranged from 0.05 to 0.4 m/s. In an in situ CC calibration in five Swiss rivers employing SDB-RPS disks covered with a diffusion-limiting PES membrane, the sampling rates did not depend on the variation of flow velocities between 0.05 m/s and 0.8 m/s.[36] Considering further the generally assumed reduction in uptake rate for flow velocities below 0.1 m/s, our results from stream 2 (v = 0.05 m/s; see also Table SM-5) might slightly underestimate the TWA pesticide concentrations.

River Mulde drains the Saxon part of the Ore Mountains northwards. On its further way to and through Grimma, it receives run-off from agricultural areas. Moreover, our sampling site is receiving water from the sewage treatment plant of Grimma, and thus is subject to additional urban impact. Here, 33 pesticides were detected, more than in any other field site of this study.

The highest concentrations were found for 2-hydroxyterbutylazine (2-OH-TBZ, 15.1 ng/L) and 2-OH-ATZ (9.8 ng/L), exceeding their parent compounds terbutylazine (TBZ, 3.0 ng/L) and ATZ (2.3 ng/L) by factors of 5 and 4.3, respectively. Moreover, parallel occurrence of deethylterbutylazine (DE-TBZ, 3.3 ng/L), deethylatrazine (DE-ATZ, 3.1 ng/L) and deisopropylatrazine (DI-ATZ, 3.7 ng/L) demonstrates metabolic dealkylation of TBZ and ATZ as additional significant degradation pathway in the field. Overall, this pattern of low parent compound vs high metabolite concentrations suggests TBZ and ATZ input at least some months before sampling, and thus reflects

also the sampling time November as compared to triazine use earlier in the year (see also below).

Further pesticides with relatively high concentrations in the river Mulde were fenuron (8.5 ng/L) and carbendazim (8.2 ng/L). Input of carbendazim could be attributed to biocide run-off from its use for wood protection or in construction materials. Fenuron is not approved as a pesticide in Germany. However, fenuron may be used as pre-emergence herbicide to free the field from weeds before sowing, which holds correspondingly for flufenacet (6.1 ng/L) and metazachlor (4.0 ng/L) with also relatively high concentrations. By contrast, isoproturon (5.6 ng/L) belongs to the herbicides used for winter grains. Overall, the November Mulde profile suggests a dominance of pre-emergence herbicides over field run-off in autumn.

Our sampling sites in the six small streams (streams 1 – 6) in Lower Saxony and Saxony-Anhalt (Germany) were located in agricultural areas, and thus are subject to run-off of pesticide residues. An additional stream in a forest without agricultural impact was included as reference site (stream_Ref). The samplers were deployed and processed in duplicates, except for site stream 3, where one sampler got lost during deployment.

Between 5 and 22 compounds could be detected in these small streams. In the reference stream, 6 herbicides and 1 insecticide (imidachloprid) were found in low concentrations of 0.8 to 2.5 ng/L, including some banned triazines (Table 2). By contrast, the sampling site of stream 1, located about 1 km downstream of the reference site, contained only 5 pesticides in an again low concentration range of 0.8 – 3.6 ng/L,

with the banned dichlorvos as only insecticide. This indicates a generally low field run-off into stream 1 where agriculture makes up only 36% of the primary land use (Table SM-5). The significantly higher portion of agricultural land use of ca. 85% at streams 2 (seven different crops), 3 (five crops) and 6 (four crops) is reflected by correspondingly larger numbers of 21, 22, and 20 waterborne pesticides with TWA c_w values of 0.6 – 49.4 ng/L, 1.1 – 30.6 ng/L and 0.3 – 9.3 ng/L, respectively. Interestingly, the top-concentration pesticide at each of these 3 streams is low elsewhere: Herbicide MCPA showed 49.4 ng/L in stream 3 but otherwise ≤ 4.1 ng/L, the TBZ hydrolysis product 2-OH-TBZ was found at 30.6 ng/L in stream 2 with levels ≤ 3.7 ng/L in the other streams (but 14.1-15.6 ng/L in the rivers Mulde and Havel, see above and below), and the ATZ metabolite DI-ATZ was detected in stream 6 at 9.3 ng/L with concentrations ≤ 2.0 ng/L elsewhere (but 3.7 ng/L in the river Mulde, see above). Streams 4 and 5 with agricultural land uses of 79% (3 crops) vs 62% (3 crops) yielded 7 and 11 pesticides at TWA concentrations of 0.5 – 4.4 ng/L and 0.5 – 12.4 ng/L, respectively. Overall our results show that the number of waterborne pesticides reflects the extent of agricultural use, and discriminates ≥ 85% agriculture (20-22 pesticides) from < 80% (5-11 pesticides). In contrast to the river Mulde sampled in November, the small streams are dominated by broad leave herbicides such as MCPA (49.4 ng/L in stream 3), metamitron (17.2 ng/L in stream 2) and chloridazon (8.9 ng/L in stream 2), by insecticides such as the neonicotinoid chlothianidin (12.6 ng/L in stream 3), and by post-emergence herbicides such as mecoprop (12.4 ng/L in stream 5 and 13.5 ng/L in the river Havel in July).

The July sampling in the river Havel (H-Jul) in the city Potsdam (Brandenburg, Germany) yielded 26 different pesticides at levels of 0.3 – 15.7 ng/L. In August, (H-Aug), only 18 pesticides could be detected at mostly slightly lower concentrations (0.2 – 15.4 ng/L). In both July and August, the top 4 concentrations were 15.7 vs 5.0 ng/L (simazine), 14.1 vs 15.4 ng/L (2-OH-TBZ), 13.5 vs 10.2 ng/L (mecoprop), and 10.7 vs 9.8 ng/L (terbutryn). The latter indicates that among the overall low concentrations, the triazine herbicides and mecoprop as phenoxyacetic acid herbicide play a major role. Since the river Havel site is in a highly urbanized region, its pesticide profile may result from both agricultural and private applications.

Overall, only 36 of the 38 laboratory-calibrated pesticides and pesticide transformation products were analysed in the field, because quinmerac and bentazone did not provide linear uptake kinetics for the three weeks of deployment. All compounds could be detected at our 10 field sites at least once. Among them are also ATZ and associated transformation products as mentioned above, although ATZ had been banned in Germany already in 1991.

The concentration patterns of ATZ, TBZ and their transformation products in the river Mulde (Grimma, Saxony) have already been discussed above. Regarding the agricultural streams in Lower Saxony and Saxony-Anhalt, the highest ATZ concentration could be found in stream 5 (2.8 ng/L, **Table 2**). This corresponds to literature data of agricultural catchments in Saxony-Anhalt, where ATZ could be found in mean concentrations of 2 ng/L to 3 ng/L in two sampling periods in May and July 2013.[22] In natural waters, ATZ may be hydrolyzed at reasonable rates to 2-OH-ATZ.[30] In addition and as mentioned above, ATZ is biotransformed to DE-ATZ and DI-ATZ, [29, 31]

both of which are subject to further degradation.[37] Thus increasingly older ATZ input will result in increasing abiotic and metabolic degradation, and probably also in increasingly further degradation of the metabolites DE-ATZ and DI-ATZ. From this viewpoint, streams 3 and 5 represent sites with older vs recent ATZ input (**Table 2**): Stream 3 features a relatively small total ATZ-related loading with 4.5 times more 2-OH-ATZ than ATZ (2.7 ng/L vs 0.6 ng/L), only 1.2 ng/L DE-ATZ and no DI-ATZ. By contrast, stream 5 contains as much atrazine as 2-OH-ATZ (2.8 ng/L) and almost three times more DE-ATZ (7.9 ng/L), and still a significant DI-ATZ concentration (2 ng/L).

At streams 2 and 6, atrazine hydrolysis has proceeded to intermediate extents (concentration ratios 2-OH-ATZ:ATZ = 2.8 and 2.2, respectively). At the same time, the DI-ATZ concentration is much larger at stream 6 than at stream 2 (9.3 ng/L vs 2.0 ng/L). This might reflect a correspondingly higher metabolic capacity of bacteria and plants at stream 6, or a longer exposure time for further degradation than at stream 2.

Comparison of H-Jul with H-Aug is also in line with this transformation rate reasoning: H-Jul still contains minor concentrations of ATZ, DE-ATZ and DI-ATZ that are gone one month later with a parallel increase of the 2-OH-ATZ concentration. Note further that the maximum DE-ATZ and DI-ATZ concentration detected with AD-CC surpass their previously reported concentration ranges of 2 – 4 ng/L and 6 – 8 ng/L, respectively, in agricultural catchment areas of Saxony-Anhalt.[22] Finally, stream_ref with a moderate 2-OH-ATZ concentration as only atrazine-related loading is again likely a site with old ATZ input, since all ATZ, DE-ATZ and DI-ATZ have already been degraded below the analytical detection limit.

Besides ATZ, our AD-CC sampling detected sebuthylazine, simazine, propazine and terbutryn as also banned herbicides (**Table 2**), keeping in mind that terbutryn is still allowed as a biocide in storefront painting. Interestingly, simazine was found in a high amount in H-Jul (15.7 ng/L) that reduced to about 1/3 after one month (H-Aug: 5 ng/L), probably reflecting a corresponding degradation through hydrolysis and metabolic dealkylation. H-Jul also contained a substantial concentration of terbutryn that was similar to the value of H-Aug (10.7 ng/L vs 9.8 ng/L). Calculated hydrolysis rates at pH = 7 and T = 25°C of triazine herbicides do not exceed 62 d (Table SM-1)[38], further supporting the likeliness of recent input in the streams, since transformation rates can be increases considerably with increasing humic acid content and decreasing pH.[30]

TBZ as only approved triazine herbicide of our study has been detected in the river Havel up to 4.5 ng/L (H-Jul) parallel to its hydrolysis product 2-OH-TBZ (Table 2). The latter was found at still larger concentrations in stream 2 (30.6 ng/L vs 2.3 ng/L), H-Jul (14.1 ng/L vs 4.5 ng/L), H-Aug (15.4 ng/L vs 2.8 ng/L) and Mulde (15.1 ng/L vs 3.0 ng/L, see above). Moreover, only the rivers Havel and Mulde also contained the metabolite DE-TBZ at low concentrations (H-Jul: 5.9 ng/L, H-Aug: 3.8 ng/L, Mulde: 3.3 ng/L). These concentration patterns suggest a substantial former terbutylazine input at stream 2 where probably DE-TBZ has already been degraded further, and again substantial but more recent inputs at the rivers Havel and Mulde.

The rivers Havel and Mulde also contained the phenylurea-based herbicides diuron, fenuron and isoproturon that are no longer allowed for agricultural use. The largest isoproturon concentration, however, was detected in stream 3 (15.3 ng/L), suggesting a substantial recent input of this compound. While the input of isoproturon in agricultural

streams probably comes from herbicide use, the input of diuron may also result from leaching of biocide products for construction materials.

The pyridazon derivative chloridazon as further herbicide without admission has been found only in streams 2 and 3, and Mulde, and only stream 1 contained the neurotoxic insecticide dichlorvos that is no longer admitted in agriculture and as biocide.

Since September 2018, the neonicotinoids clothianidin, imidacloprid and thiamethoxam are no longer admitted for agricultural applications in the field.[39] Of these three insecticides, clothianidin was detected in streams 2 (9.2 ng/L) and 3 (12.6 ng/L) at the concentration levels above the regulatory acceptable concentration (RAC) of 7 ng/L as derived by the German Environmental Agency (UBA). Provided that the compounds are not applied anymore, the concentrations will gradually drop below LOQ, as indicated in the Havel, where concentrations in August are below concentrations in July for monitored neonicotinoids (**Table 2**). The concentration ranges of the target compounds in all field samples, including RAC-values and median can be found in Figure SM-4.

Overall, 15 of the 31 pesticides (augmented by 5 transformation products) detected through AD-CC passive sampling have no agricultural approval in Germany. Generally, the detected pesticide profiles reflect agricultural activity and are governed by the following compounds: triazine herbicides and their abiotic and biotic transformation products (0.3 – 30.6 ng/L), neonicotinoid insecticides (0.2 – 12.6 ng/L), and the phenoxyacetic acid herbicide mecoprop (1.1 – 13.5 ng/L). Further individual hot spots occur for the triazinone herbicide metamitron (stream 2: 17.2 ng/L, stream 2: 13.8 ng/L), for the banned phenylurea herbicide isoproturon (stream 3: 15.3 ng/L), and for the

phenoxyacetic acid herbicide MCPA with the overall largest concentration (stream 3: 49.4 ng/L). A final peculiarity concerns the banned pyridazone herbicide chloridazon at streams 2 (8.9 ng/L) and 3 (5.3 ng/L).

The following 9 bioactive agents of our current study were also detected in a European river study in 2008 at typically higher concentrations:[40] 2,4-D, mecoprop, ATZ, DE-ATZ, simazine, TBZ, DE-TBZ, diuron and isoproturon (Table SM-6). The generally reduced levels reported now may reflect legislative actions as is illustrated with diuron (41 ng/L in 2008[40] vs 2.9 ng/L in 2018) and isoproturon (52 ng/L in 2008[40] vs 4.8 ng/L in 2018). For these herbicides, the agricultural approval in Germany expired in 2007 and 2016, respectively, thus explaining their reduced environmental levels since then.

Pesticide concentrations in the rivers Havel and Mulde do not exceed 20 ng/L, indicating similar concentrations as in other German and European water bodies.[41–43] Diuron, isoproturon, mecoprop, 2,4-D and ATZ could be detected in the river Mulde in similar concentrations as in the river Danube during the Joint Danube Survey 2 (Aug-Sep 2007).[41] DE-ATZ, DE-TBZ and TBZ were found in river Danube in concentrations between ~15 ng/L (TBZ) and ~25 ng/L (DE-TBZ) compared to lower concentrations in the river Mulde (TBZ: 3.0 ng/L, DE-TBZ: 3.3 ng/L). However, a recent review by Sousa *et al.* (2020) showed that local maximum concentrations may be as high as 45 µg/L for ATZ and 1µg/L for diuron in surface waters across the world.[5] While the concentrations monitored in this study may be below seasonal maxima in spring,[42] it still shows a generally low contamination of the rivers Havel and Mulde.

Table 2: TWA concentrations of pesticides and metabolites in field samples [ng/L] taken in June 2018 (streams in Lower Saxony and Saxony-Anhalt, Germany), July and August 2018 (river Havel) as well as November 2018 (river Mulde).

	Saxony		Lower Saxony			Saxony-Anhalt			Brandenburg		
Compound	**Mulde**	**Stream_Ref**	**Stream 1**	**Stream 2**	**Stream 3**	**Stream 4**	**Stream 5**	**Stream 6**	**H-Jul**	**H-Aug**	**Approval***
Carbamates											
Carbendazim	8.2			1.2	0.9			1.0	3.5	2.2	NA[3]
Pirimicarb	2.7			3.6	0.6						A
Chloroacetanilides											
Dimethachlor	2.7										A
Metazachlor	4.0			3.1	2.1			1.5			A
Metolachlor	1.7								1.3		A
Miscellaneous											
Chloridazon	1.2			8.9	5.3						NA
Dichlorvos			3.6					0.3	0.3		NA
Ethofumesate	1.7			2.0		1.9	2.1	1.8	2.0	0.5	A
Flufenacet	6.1			2.9	0.7			0.6			A
Neonicotinoids											
Clothianidin	1.8			9.2	12.6	4.4		3.5			NA [1,2]
Imidacloprid	3.9	0.8		3.7	3.1		0.5	5.6	3.2	2.6	A[2]
Thiacloprid	1.5							0.5	0.6	0.2	A[2]
Thiamethoxam	1.6				0.7			0.9	0.8		NA [1,2]
Phenoxyacetic acid derivatives											
2,4-D	1.0				1.0				0.8	1.0	A
2,4-DB											NA
Dichlorprop	1.1			1.8		0.9	1.7	1.9	1.4	1.1	A
MCPA	4.1		1.9	1.9	49.4		2.8		1.6	4.1	A
MCPB	3.1	1.2	1.6							3.1	NA
Mecoprop	5.7			1.1	1.3		12.4	0.9	13.5	5.7	A
Phenylureas											
Diuron	3.9						0.9	1.1	6.0	4.2	NA[3]
Fenuron	8.5								2.0	0.4	NA
Isoproturon	5.6			1.2	15.3				3.6	2.7	NA
Triazines											
Atrazine	2.3			1.3	0.6	1.3	2.8	1.3	0.7		NA
Deethylatrazine	3.1			1.2	1.2	2.7	7.9	1.7	0.8		M
Deisopropylatrazine	3.7		0.8	2.0			2.0	9.3	0.8		M
2-Hydroxyatrazine	9.8	2.0		3.6	2.7		2.8	2.8	5.4	6.7	M
Propazine	2.4										NA
Sebuthylazine	2.1	0.8		1.1	1.0			1.0	0.3		NA
Simazine	1.9	2.5							15.7	5.0	NA
Terbutylazine	3.0	1.5		2.3	2.1	1.7		2.5	4.5	2.8	A
Deethylterbutylazine	3.3								5.9	3.8	M
2-Hydroxyterbutylazine	15.1	2.5	2.0	30.6	3.7	1.2	1.9	1.6	14.1	15.4	M
Terbutryn	3.8			2.2	0.9			0.8	10.7	9.8	NA[3]
Triazinones											
Lenacil	3.2			2.7	0.6				0.5		A
Metamitron	1.3			17.2	13.8						A
Metribuzin									0.8		A

** in Germany[44] A = approved; NA = not approved; M = Metabolite*
[1] approved at the time of the study; [2] approved as a biocide; [3] approved as a biocide at the time of the study
Streams 1 – 6 are located in agriculturally shaped regions, river Mulde sampling site is shaped by agriculture and small cities; river Havel site is located in a highly urbanized region

Passive sampling enables to detect bioactive agents at concentrations far below the limit of quantification in conventionally taken water samples (Table SM-3) because the minimal quantifiable water concentration is governed by the sampling rate R_s and the exposure time t. This is also demonstrated by the low concentrations displayed in **Table 2**. However, site-specific hydrodynamics and sampler fouling may confound the

applicability of laboratory calibration to the situation in the field, adding uncertainty contributions to the conventional standard errors derived from the replicate analysis. In this context, a possible way forward appears to be the parallel exposure of at least two different passive sampling devices, which will be subject of a future investigation.

3.3. Extended Target Screening

The extended target screening was conducted to evaluate the application range of AD-CC with samples from the river Havel. 290 compounds could be annotated by calibration standards. Annotated compounds were sorted by use pattern and hydrophobicity in terms of log K_{ow}. The samplers collected 286 and 264 compounds in two consecutive sampling periods in July and August 2018, with log K_{ow} mean values and 90%-quantiles of 2.13 and 2.17 and of 4.5 and 4.7, respectively (Figure SM-5). These results indicate similar uptake conditions in both sampling periods and show that AD-CC can sample polar organic compounds efficiently.

71% of the detected analytes are pharmaceuticals, pesticides and industrial chemicals (Figure SM-6). At least 84 different pharmaceuticals could be detected in each sample, which form the largest group. In a similar screening of a South African river in 2020, pharmaceuticals also accounted for the majority of compounds detected in an urbanized river catchment (49%).[45] While HR-MS screens of AD-CC in other studies mainly focused on pharmaceuticals,[45,24,20] this study shows that AD-CC can be applied as a passive sampler for polar organic compounds in general and also collects pesticides

and other compounds of emerging concern, including stimulants such as caffeine and organophosphorous flame retardants (Table SM-7).

Compound concentrations in the sampler (m_s) range from 0.1 ng/disk to 21,000 ng/disk with 50% of the detected compounds showing concentrations below 10 ng/disk. These results indicate that the majority of micropollutants is at only low ng/L-concentrations in the surface water. The mean standard error of m_s across all detected compounds is 25%, demonstrating the robustness of AD-CC across a broad concentration range.

4. Conclusions

AD-CC shows great potential as a passive sampler for polar organic pesticides in surface waters with log K_{ow} values up to ca. 4.5. Mean standard errors of m_s (compound mass sampled) commonly do not exceed 25%, making AD-CC a robust monitoring instrument. As compared to ED-CC, the longer linear uptake phase of AD-CC of up to 3 weeks offers larger flexibility regarding exposure times for both research and regulatory monitoring programs. As demonstrated for agricultural streams, passive sampling offers an efficient means to analyse herbicides and insecticides as related to predominant land use and associated run-off. Moreover, parallel analysis of pesticide transformation products enables to draw conclusions about old vs recent input. In this context, information about the levels of banned pesticides in surface waters appears to be particularly valuable, and allows one to assess respective regulatory measures regarding actual environmental concentrations. The further development and use of passive sampling, however, would profit from systematic studies employing different

samplers under otherwise identical conditions as reported recently,[43] thus informing about additional potentially confounding factors beyond sampler-specific standard errors.

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ABBREVIATIONS

ED, Empore Disk; AD, Atlantic Disk; CC, Chemcatcher; HLB, Hydrophilic Lipophilic Balance; SDB-XC, styrene-divinylbenzene; SDB-RPS, styrene-divinylbenzene reversed phase sulfone.

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Highlights

- First laboratory calibration of pesticides uptake in Atlantic HLB-L Disk passive sampler
- Linear uptake span generally three weeks
- Analysis of metabolite patterns allows discrimination between old vs new input
- Extended target screening shows broad application range for Atlantic HLB-L Disk

Credit Author Statement

Mara Grodtke: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. **Albrecht Paschke**: Conceptualization, Methodology, Writing – Original Draft, Writing – Review & Editing, Supervision. **Julia Harzdorf**: Methodology, Formal analysis, Investigation. **Martin Krauss**: Methodology, Writing – Original Draft. **Gerrit Schüürmann**: Conceptualization, Resources, Writing – Original Draft, Writing – Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: