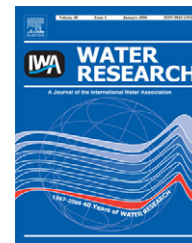


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Performance of the Chemcatcher[®] passive sampler when used to monitor 10 polar and semi-polar pesticides in 16 Central European streams, and comparison with two other sampling methods

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ABSTRACT

We investigated the performance of the Chemcatcher[®], an aquatic passive sampling device consisting of a sampler body and an Empore[®] disk as receiving phase, when used to monitor acetochlor, alachlor, carbofuran, chlorfenvinphos, α -endosulfan, fenpropidin, linuron, oxadiazon, pirimicarb and tebuconazole in 16 Central European streams. The Chemcatcher[®], equipped with an SDB-XC Empore[®] disk, detected seven of the aforementioned pesticides with a total of 54 detections. The time-weighted average (TWA) concentrations reached up to 1 $\mu\text{g/L}$ for acetochlor and alachlor. Toxic units derived from these concentrations explained reasonably well the observed ecological effects of pesticide stress, measured with the SPEAR index. In a follow-up analysis, we compared the Chemcatcher[®] performance with those of two other sampling systems. The results obtained with the Chemcatcher[®] closely matched those of the event-driven water sampler. By contrast, the TWA concentrations were not significantly correlated with concentrations on suspended particles. We conclude that the Chemcatcher[®] is suitable for the monitoring of polar organic toxicants and presents an alternative to conventional spot sampling in the monitoring of episodically occurring pollutants.

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1. Introduction

The monitoring of pesticide concentrations in surface waters is an inevitable step for the environmental risk assessment of pesticides. For these compounds, field runoff represents a relevant input path into streams in agricultural

areas (Liess et al., 1999; Neumann et al., 2002). Runoff events occur discontinuously in association with heavy precipitation, and runoff-related pesticide exposure may have adverse effects on invertebrate communities (Leonard et al., 2000; Liess and von der Ohe, 2005). Since most pesticide concentrations during runoff events decrease to

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background levels within hours to a few days, routine water monitoring which mainly relies on spot (bottle) sampling at fixed intervals is likely to miss a great proportion of relevant events (Richards and Baker, 1993; Leu et al., 2004). Hence, environmental monitoring techniques are needed that allow for detection of runoff-related peak exposure and that are labour- and cost-efficient at the same time.

Continuous water sampling represents an alternative to spot sampling. Throughout the last decade, passive sampling devices using various receiving phases have been employed successfully for continuous monitoring of various pollutants in surface waters (Stuer-Lauridsen, 2005; Vrana et al., 2005). The Chemcatcher[®] passive sampler with polar receiving phase and the polar organic chemical integrative sampler (POCIS) performed well in the monitoring of polar organic contaminants (Escher et al., 2006; Alvarez et al., 2007). Nevertheless, there is a paucity of studies addressing the monitoring of short-term pollution events with passive samplers (Greenwood et al., 2007). Furthermore, to our knowledge, only one study demonstrated a relationship between pesticide concentrations determined by passive samplers and effects on aquatic communities (Leonard et al., 2000). The establishment of such a relationship is hampered by the fact that time-weighted average (TWA) concentrations are obtained from passive sampling devices, whereas peak concentrations are required to assess potential acute ecotoxicological effects. In this study we present results of a field study at 16 sampling sites using the Chemcatcher[®] passive sampler to detect the polar and semi-polar pesticides acetochlor, alachlor, carbofuran, chlorfenvinphos, α -endosulfan, fenpropidin, linuron, oxadiazon, pirimicarb and tebuconazole. The compounds were chosen on the basis of their ecotoxicological relevance in the sampling region (Schäfer et al., 2007a). In addition, we examine the extent to which the TWA concentrations can be related to a community-based biotic index—the Species At Risk (SPEAR)-index—designed to detect effects of pesticides on benthic invertebrates (Liess and von der Ohe, 2005).

Since several sampling systems have been proposed to assess runoff-related pesticide exposure, there is also a need to compare the performance of different sampling systems. Therefore, another objective of this study was to compare the performance of the Chemcatcher[®] with the performances of two other sampling systems: an event-driven water sampler (EDS) and a suspended-particle sampler (SPS). (Technical drawings of all sampling methods can be found in the supplementary data.) Both methods have been proposed and used to catch runoff events in previous studies (Liess et al., 1996, 1999; Schulz et al., 2001; Liess and von der Ohe, 2005) and were deployed at the same sampling sites as the passive samplers in this study (Schäfer et al., 2007a,b). Comparison of the Chemcatcher[®] to these sampling methods comprised the following criteria: (1) number of pesticides detected and (2) the total number of detections above the limit of quantitation. Since sampling methods should deliver results that are relevant to assess effects on biota, we included as criteria also (3) the ability to explain variation in the SPEAR index.

2. Materials and methods

2.1. Study area

Brittany, located in northwestern France, was chosen as the sampling region since (1) agriculture is the predominant land-use type there with 23.5% of the area (27,510 km²) being used for corn (19.2%), vegetable (2.6%), oil-seed (1.2%) and potato (0.5%) production and (2) in Western Europe pesticide usage is the highest globally in terms of expenditures per area (Oerke and Dehne, 2004). A total of 16 sampling sites in small agricultural streams (max. width: 5 m, max. depth: 0.8 m) were selected on the basis that they were expected to exhibit a gradient in pesticide contamination (Schäfer et al., 2007a).

2.2. Preparation, deployment and extraction of the passive sampler

The Chemcatcher[®] passive sampling device (University Portsmouth, UK; commercially available at Alcontrol AB, Linköping, Sweden) was employed for continuous water monitoring as described by Kingston et al. (2000). The Chemcatcher[®] consists of a polytetrafluoroethylene (PTFE) sampler body and, for the purpose of this study, was equipped with SDB-XC Empore[®] disks (3M, Neuss, Germany) as the receiving phase (47 mm diameter; 15.9 cm² surface area) containing polystyrene-divinylbenzene (PS-DVB) as sorbent.

Before use, the SDB-XC Empore[®] disk was conditioned with 10 mL acetone (HPLC-grade), 10 mL 2-propanol (analytical grade) and 10 mL methanol (HPLC-grade) obtained from Merck (Darmstadt, Germany). The conditioned disks were placed in the Chemcatcher[®] body, which was subsequently filled with purified water, closed and stored in zip-lock bags at 4 °C until exposure (<48 h). To obtain a rapid response to concentration changes, no diffusion-limiting membrane was used. Procedural blanks were stored non-exposed throughout the whole study period.

The Chemcatcher[®] devices were deployed at the 16 sampling sites on 9–11 May for 10–13 days (Fig. 1), prior to a period with expected heavy precipitation according to the local weather forecast (www.meteofrance.com). The samplers were fixed to steel bars approximately 15 cm below the water surface. The open side of the Chemcatcher[®] was sealed with a copper mesh (mesh size 5 mm) to prevent mechanical damage and suppress biofouling (Vrana et al., 2005). It was directed towards the stream bottom. Four sites were equipped in duplicate and one in triplicate to assess the variability of the pesticide uptake. A field blank was exposed to the air during deployment and retrieval of samplers to account for potential airborne pollution.

After exposure, the passive samplers were filled with stream water from the respective site, closed and stored in zip-lock bags at 4 °C in the dark. In the laboratory, the SDB-XC Empore[®] disks were carefully taken off the PTFE body, dried under vacuum using a vacuum manifold for about 15 min and subsequently eluted twice with 10 mL acetonitrile/methanol. The eluate was gently evaporated to dryness under nitrogen at 30 °C in a 200 mL evaporation vial using a TurboVap 2 concentration workstation (Zymark, Hopkington, USA) and

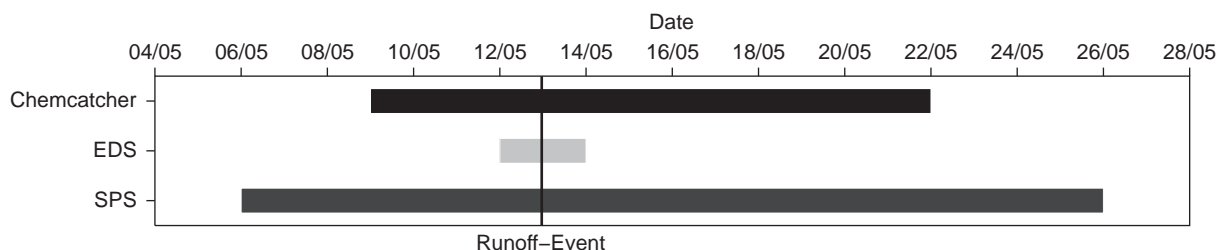


Fig. 1 – Sampling scheme for the three monitoring methods in 16 French streams. “Runoff-event” indicates a heavy precipitation event (> 10 mm/day).

Table 1 – Physicochemical and analytical data for 10 measured pesticides

Compound	Type ^a	Class ^a	Log _{K_{ow}} ^b	Log _{K_{oc}} ^b	LOQ CC (ng/L) ^{c,d}	LOQ EDS (ng/L) ^c	LOQ SPS (μg/kg) ^{c,e}	LOQ calc. (μg/kg) ^{c,f}	LC50 (μg/L) ^{a,g}
Acetochlor	H	Chloroacetamide	2.39	2.32	5.1	25	12.5	0.26	9000
Alachlor	H	Chloroacetamide	3.52	2.28	5.4	25	12.5	0.24	10,000
α-Endosulfan	I	Organochlorine	3.83	4.13	3.6	25	12.5	16.86	75
Carbofuran	I	Carbamate	2.32	1.75	10.4	25	12.5	0.07	38.6
Chlorfenvinphos	I	Organic phosphorous acid	3.10	2.47	5.2	25	12.5	0.37	0.3
Fenpropidin	F	Piperidine	2.90 ^a	3.20 ⁱ	4.1	25	12.5	1.98	500
Linuron ^h	H	Urea derivative	3.20	2.70	4.3	25	12.5	0.63	120
Oxadiazon	H	Oxadiazole	4.80	3.51	3.5	25	12.5	4.04	2400
Pirimicarb	I	Carbamate	1.70	1.90	4.5	25	12.5	0.10	17
Tebuconazole	F	Triazole	3.70 ^a	3.50 ⁱ	6.1	25	12.5 ^j	3.95	4200

^a Taken from Tomlin (2003), I = insecticide, H = herbicide, F = fungicide.

^b Taken from Sabljic et al. (1995).

^c LOQ = limit of quantification for a sample obtained with the respective method.

^d CC = Chemcatcher[®]; computed for 14-day exposure.

^e For extraction of 10 g of suspended particles.

^f Sample LOQ for suspended particles that would correspond to the level of the EDS LOQ assuming equilibrium partitioning, computed according to $LOQ_{calc.} = LOQ_{EDS} \cdot K_{oc} \cdot f_{OC}$, where f_{OC} is the mass fraction of organic carbon (assuming $f_{OC} = 5\%$).

^g LC50 for *Daphnia magna*.

^h Quantificated as 3,4-dichloroaniline.

ⁱ Estimated with Chemprop 4.1 (<http://www.ufz.de/index.php?en=6738>).

^j 25 and 100 for some samples with high matrix interference.

redissolved with 200 μL acetonitrile. Prior to analysis, 5 μL triphenyl phosphate (TPP) was added as internal standard (IS).

2.3. Chemical analysis

The selected compounds (Table 1) were quantified using an Agilent 6890N (Agilent Technologies Germany, Boeblingen, Germany) gas chromatograph (GC) equipped with a MPS2 autosampler, a CAS4 inlet (both from Gerstel, Mühlheim a.d. Ruhr, Germany) and an Agilent 5973 mass selective detector (MSD). The limit of quantification (LOQ) of the GC-MSD was 125 pg/μL for all compounds. The sample LOQs differed between the sampling methods and between compounds for the Chemcatcher (Table 1). Typical total ion chromatograms are given in Fig. 2.

2.4. Calculation of passive sampler TWA concentrations

From the field-exposed passive samplers, the accumulated mass of each compound per sampler is obtained. To calculate

TWA concentrations, a substance-specific sampling rate R_s , expressed in equivalent volume of sampled water per day, is required. For the compounds of this study, the sampling rates were previously determined in a laboratory flow-through experiment and found to range from 0.1 to 0.5 L/day (Gunold et al., 2007). In addition, this calibration study showed that the Chemcatcher[®] remained in the linear integrative uptake regime for up to 14 days. Using the sampling rates of this study, the TWA concentrations for the sites in our study were calculated according to

$$C_w = \frac{m_s}{R_s t}, \quad (1)$$

where C_w is the TWA concentration of the respective analyte in the water phase in the dimension mass/volume and m_s is the accumulated mass after exposure time t . The procedural blank and the field blank yielded zero background contamination and had therefore not to be considered in Eq. (1).

The calculated TWA concentrations should be regarded as approximation only, because between-site variation in water

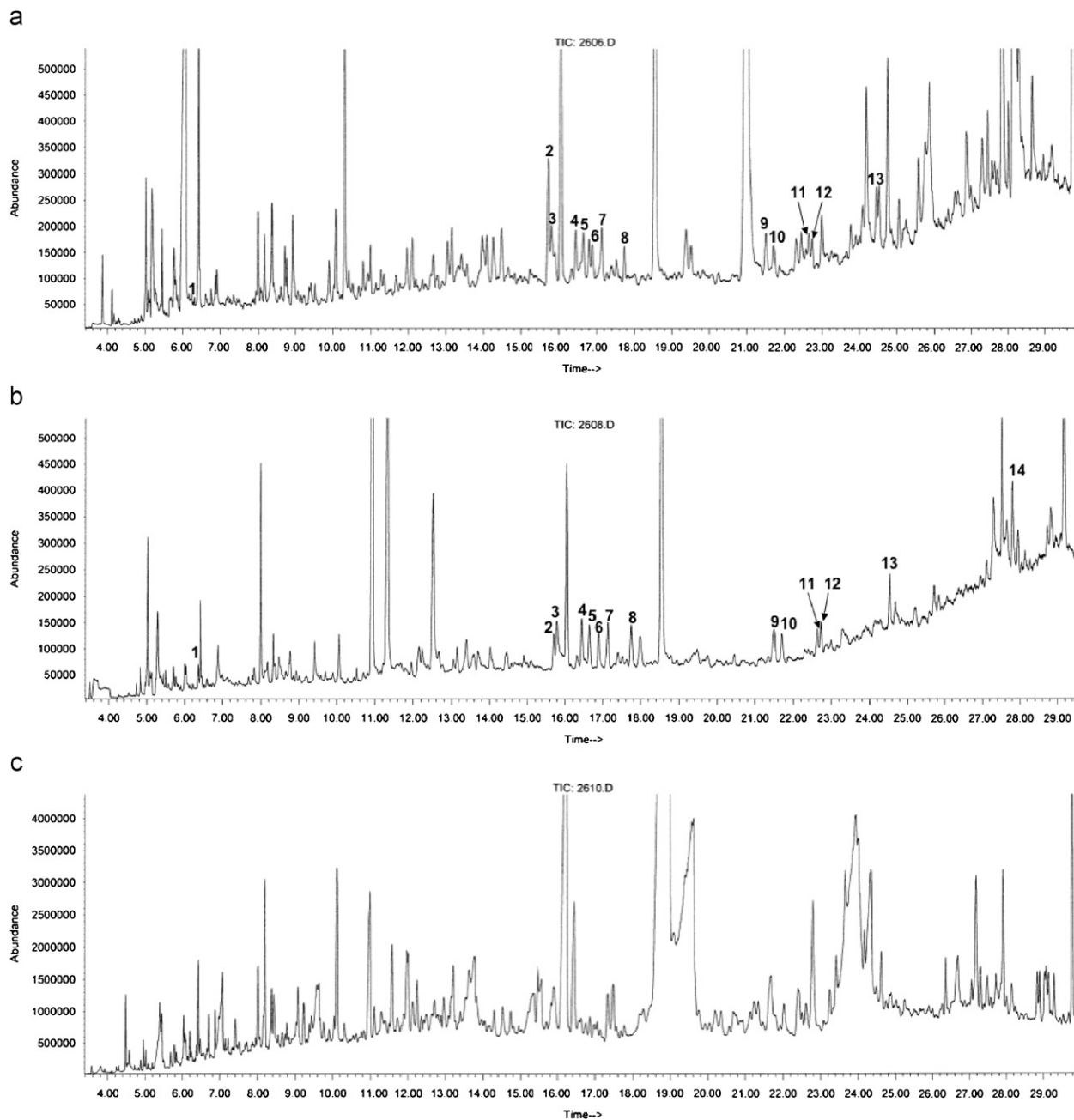


Fig. 2 – Typical total-ion chromatograms for (a) the event-driven water sampler (EDS), (b) the Chemcatcher[®], and (c) the suspended-particle sampler (SPS). The samples were spiked with 1 µg/L (SPS 100 µg/kg) of pesticide standards. Deuterated internal standards were only used for comparison of the EDS and Chemcatcher[®]. Please note the different scaling of the y-axis for the SPS chromatogram. Analytes: 1: carbofuran, 2: pirimicarb D6, 3: pirimicarb, 4: acetochlor D11, 5: acetochlor, 6: alachlor D13, 7: alachlor, 8: fenpropidin, 9: chlorfenvinphos D10, 10: chlorfenvinphos, 11: α -endosulfan D4, 12: α -endosulfan, 13: oxadiazon, 14: tebuconazol.

temperature and biofouling were not taken into account, as the performance reference compound (PRC) concept (Huckins et al., 2002) was not applicable (Gunold et al., 2007).

2.5. Linking exposure to the SPEAR index

We examined the extent to which the TWA concentrations determined with the Chemcatcher[®] can explain variation in the SPEAR index. Briefly, the SPEAR index predicts the effects

of organic toxicants on the invertebrate community of a site, based upon traits of benthic invertebrates such as voltinism, migration potential, emergence time and physiological sensitivity (Liess and von der Ohe, 2005). Practically, these traits are used to classify the observed macroinvertebrate community of each sampling site into taxa potentially sensitive or tolerant towards organic toxicants. Subsequently, the SPEAR index value for a respective site is derived by computing the relative abundance of sensitive species in a community.

Details on the sampling of the benthic invertebrates and on the computation of the SPEAR index are given in Schäfer et al. (2007a).

To assess and standardize the toxicity of the measured TWA concentrations, a log-transformed maximum toxic unit (TU) was computed using the 48-h acute median lethal concentration (LC50) for *Daphnia magna* (Table 1) as described by Schäfer et al. (2007a). A TU value of -5 was assigned to a site if no pesticide was found, corresponding to unpolluted sites in a previous study (Liess and von der Ohe, 2005).

2.6. Description of the EDS

The EDS was designed to catch peak concentrations during pesticide runoff. The sampling system set into the streams consisted of a 1-L glass bottle fixed to a steel bar and was mounted approximately 5 cm above normal water level (Liess et al., 2001; Schulz et al., 2001). After a heavy rain event (>10 mm precipitation/24h) the filled sample bottles were retrieved and water samples were solid-phase-extracted using 6 mL Chromabond HR-P columns containing 500 mg of PS-DVB, purchased from Macherey-Nagel (Düren, Germany), according to the method described in Schäfer et al. (2007a). The eluates were treated as described for the Chemcatcher[®]. The EDS monitoring results reported here refer to a single heavy-rain event (>10 mm/day) during the study period that occurred between 12 and 13 May (Fig. 1). The TUs of this method were taken from Schäfer et al. (2007a).

2.7. Description of the SPS

The SPS was designed to sample suspended particles and consisted of a 3-L sedimentation vessel that was buried in the streambed. Suspended particles that entered therein could settle down (Liess et al., 1996). The sampled suspended material was collected at 2-week intervals, freeze-dried and passed through a 2-mm sieve to remove needles, sticks and leaf parts. Approximately 10 g (dry weight) of the sample was extracted using an accelerated solvent extraction (ASE 200 system from Dionex, Idstein, Germany; extraction parameters: two 6-min cycles with ethyl acetate–acetone (2:1) at 110 °C and 11 MPa) with subsequent size exclusion chromatography (SEC) cleanup (Biobeads S-X3 cleanup column from Antec GmbH, Sindelsdorf, Germany) as described by Schäfer et al. (2007b). Due to matrix interferences the collected fraction in SEC was not evaporated further than to 1000 μ L and, subsequently, 50 μ L TPP was added as IS. To obtain comparable data sets, we used the results of the sampling period between 6 and 23–26 May for this method (Fig. 1). A maximum sediment TU was computed from the suspended particle concentrations as described in Schäfer et al. (2007b). Log-transformed sediment TUs are referred to as STU.

2.8. Data analysis

Pearson's correlation coefficient r was calculated to indicate the similarity of two sampling methods followed by a t -test to detect significant correlations. Observations that were below LOQ for a compound at a certain site and for all sampling methods were excluded from analysis. In case an observation

below LOQ corresponded to a measurement above LOQ in another sampling method, the observation below LOQ was replaced by half the LOQ. This substitution by a constant proved to be most reliable for small data sets in a comparative study (Clarke, 1998). Linear models were constituted (1) to analyse if the linear regression for two sampling methods differed significantly between sites or compounds which were included as covariate factors, and (2) to examine the explanatory power of TU (STU for SPS) for variation in the SPEAR index.

Due to the low number of replicates (2 and 3) we calculated the relative range (RR) as dispersion measure for the TWA concentrations:

$$RR(\%) = \frac{(\max(X) - \min(X))}{\bar{X}}, \quad (2)$$

where X are the observations for the respective compound at a certain site and \bar{X} is the mean of X . The RR is a more conservative estimate of the sample dispersion compared to the relative standard deviation (RSD). All statistical computations and graphics were created with the open-source software package R (www.r-project.org) using version 2.6 (for Mac OS X, 10.4.10).

3. Results

3.1. Pesticide monitoring with the Chemcatcher[®] passive sampler

At the 16 sites, seven of the 10 target pesticides were found with the Chemcatcher[®] passive sampler (Table 2); those not detected were chlorfenvinphos, α -endosulfan and fenpropidin. Both chloroacetamide herbicides—acetochlor and alachlor—were detected most frequently above the LOQ and had the highest TWA concentrations, reaching up to 1 μ g/L. Tebuconazole and pirimicarb were found only occasionally and had the lowest TWA concentrations. The TWA concentrations exhibited high variation at three of the five sampling sites with up to 150% in terms of RR (Table 2). The other sites showed medium ($<50\%$ RR) and low ($<30\%$ RR) variation for the majority of the compounds.

The TUs for the sites ranged from -2.4 , corresponding to 1/250 the LC50 of *D. magna*, to -5 (Table 2). The TU values explained reasonably well the variation in the SPEAR index ($r^2 = 0.5$, $p < 0.01$, $n = 16$) (Table 3), indicating effects of pesticides on the abundance of sensitive invertebrate taxa.

3.2. Comparison of the three sampling methods concerning pesticide monitoring

All pesticides of the monitoring program were found in the water samples of the EDS and this sampling method yielded also a slightly higher number of total detections compared to the Chemcatcher[®] (Table 3). Nevertheless, the pesticide concentrations found by the two water sampling methods were significantly correlated ($r = 0.79$, $p < 0.01$, $n = 75$). The concentrations determined with the EDS were in general a factor of 4–5 higher than the Chemcatchers' TWA concentrations (Fig. 3). The linear regression model, encompassing EDS'

Table 2 – Time-weighted average concentrations in ng/L (\pm relative range^a where replicates available) of pesticides determined with the Chemcatcher[®] passive sampler as well as TUs and STUs for the three sampling methods^b

Site	Acetochlor	Alachlor	Carbofuran	Linuron	Oxadiazon	Pirimicarb	Tebuconazole	TU CC ^c	TU EDS ^{c,d}	STU SPS ^{c,e}
1	1158	184	124	54	10	bq	bq	–2.5	–0.4	0.7
2	14	7	21	bq	bq	bq	bq	–3.3	–2.2	–5.0
3	18	198	bq	37	bq	bq	bq	–3.5	–2.7	2.5
4	196	40	36	9	7	bq	bq	–3.0	–2.5	–2.2
5	219	96	127	48	8	bq	6	–2.5	–2.0	1.1
6	60 (\pm 148%)	12 (\pm 99%)	bq	16 (\pm 94%)	4 (\pm 72%)	5 (\pm 86%)	bq	–2.6	–2.5	–5.0
7	37	132	92	57	bq	8	bq	–3.5	–2.1	–5.0
8	454 (\pm 102%)	681 (\pm 99%)	159 (\pm 27%)	41 (\pm 116%)	9 (\pm 103%)	bq	bq	–2.4	–0.8	0.9
9	486 (\pm 29%)	1233 (\pm 14%)	52 (\pm 22%)	22 (\pm 25%)	bq	bq	15 (\pm 10%)	–2.9	–2.6	–2.0
10	388 (\pm 55%)	182 (\pm 44%)	20 (\pm 13%)	66 (\pm 48%)	26 (\pm 95%)	6 (\pm 26%)	11 (\pm 33%)	–3.3	–2.8	–4.1
11	20	14	bq	bq	bq	12	bq	–3.2	–2.6	–5.0
12	bq	bq	bq	bq	bq	bq	bq	–5.0	–5.0	–5.0
13	16 (\pm 120%)	24 (\pm 139%)	bq	bq	bq	bq	bq	–5.0	–4.7	1.0
14	bq	bq	bq	bq	bq	bq	bq	–5.0	–5.0	–2.7
15	bq	bq	bq	bq	bq	bq	bq	–5.0	–5.0	–5.0
16	bq	bq	bq	bq	bq	bq	bq	–5.0	–5.0	1.2

^a $n = 2$, except site 8 ($n = 3$). Calculated using Eq. (2).

^b bq = below limit of quantification; chlorfenvinphos, α -endosulfan and fenpropidine are not displayed because all observations were below limit of quantification.

^c Calculated with LC50 values taken from Tomlin (2003), see Table 1.

^d Calculated from data given in Schäfer et al. (2007a).

^e Calculated from data given in Schäfer et al. (2007b).

Table 3 – Comparison of the three sampling systems in 16 French sites

Sampling method	Number of different pesticides detected	Total detections above the LOQ	Explanatory power for the SPEAR index ^a
Chemcatcher [®]	7	54	$r^2 = 0.50$ ($p < 0.01$)
EDS	10	66	$r^2 = 0.38$ ($p = 0.01$)
SPS	5	22 ^b	$r^2 = 0.01$ ($p > 0.05$)

^a Linear regression with the respective TUs/STUs as explanatory variable and SPEAR as response variable.

^b Significantly lower than the total detections by the other methods in multiple comparison tests (χ^2 -test with Bonferroni correction, $p < 0.05$).

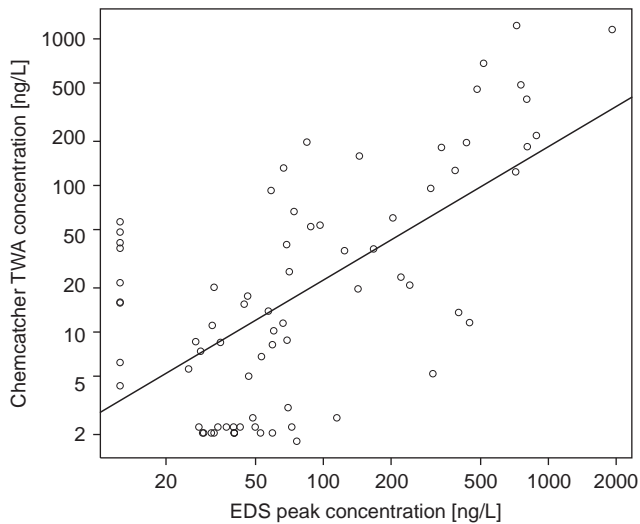


Fig. 3 – Relationship between the Chemcatcher[®] TWA concentrations and the EDS peak concentrations in 16 agricultural streams, on a double logarithmic scale.

Observations that were below LOQ for both sampling methods were excluded from analysis. Model parameters: $r^2 = 0.4$, $p < 0.01$, $n = 75$. Model parameters for non log-transformed concentration: $r^2 = 0.62$, $p < 0.01$, $n = 75$.

concentrations as explanatory variable and the Chemcatchers' concentrations as response variable, was not significantly different between sites or compounds (analysis of variance of the models with and without the covariate factors, F-test, $p > 0.05$). For the log-transformed pesticide concentrations inclusion of the covariate compounds in the linear model did increase the amount of explained variance significantly (analysis of variance, F-test, $p < 0.01$). However, separate linear regression models for each compound yielded only two significant relationships (t-test, $p < 0.05$) (Fig. 4).

In the suspended particles sampled with the SPS, only 5 of the 10 pesticides were observed; any of the compounds alachlor, carbofuran, linuron, oxadiazon and pirimicarb was found. The total number of pesticide detections (22) in the particulate phase was significantly reduced (χ^2 -test with Bonferroni correction, $p < 0.05$) compared to both water phase methods (Table 3). No significant correlations were observed between water concentrations derived from the EDS and the Chemcatcher[®] on the one hand and the suspended particle

concentrations monitored with the SPS on the other hand ($r = 0.05$ and 0.08 , $p > 0.05$, $n = 76$ and 72 , respectively).

3.3. Comparison of the three sampling methods concerning effects assessment

The STUs calculated on the basis of suspended particle concentrations were higher than the TUs based on water concentrations, with a maximum STU value of 2.5 corresponding to 321 times the LC50 for *D. magna*. For water concentrations, the TUs peaked at -0.42 , equivalent to $1/2.5$ the LC50 value for *D. magna* (Table 2). The TUs of the two water sampling methods were very similar, indicated by an r of 0.94 ($p < 0.01$, $n = 16$). The SPEAR index was reasonably well explained by the TUs of the EDS and the Chemcatcher[®], whereas no significant linear relationship was observed between STUs and SPEAR (Table 3).

4. Discussion

4.1. Using the Chemcatcher[®] for the monitoring of polar and semi-polar pesticides

The Chemcatcher[®] passive sampler equipped with a SDB-XC Empore[®] disk detected all compounds included in the monitoring program except fenpropidin, chlorfenvinphos and α -endosulfan, although these compounds were found in samples obtained by the other sampling methods. In general, the Chemcatcher[®] should be suitable for detecting these substances, as they showed above average uptake rates in the samplers' receiving phase in a calibration study (Gunold et al., 2007). The non-detections with the Chemcatcher[®] are not likely to result from too low concentrations because in the EDS samples the concentrations of fenpropidin, chlorfenvinphos and α -endosulfan were not lower than those of the other monitored compounds. An explanation for the non-detection with the Chemcatcher[®] is that the period of exposure to these pesticides was shorter than in the case of the other compounds detected, resulting in a TWA concentration below LOQ. Since we have no temporal resolution of the water concentrations over the course of the runoff event, this issue remains unresolved.

The levels of the TWA concentrations observed with the Chemcatcher[®] are in good agreement with another field study on 7 sites in southern England using the POCIS passive sampler, where concentrations up to $1 \mu\text{g/L}$ were reported for

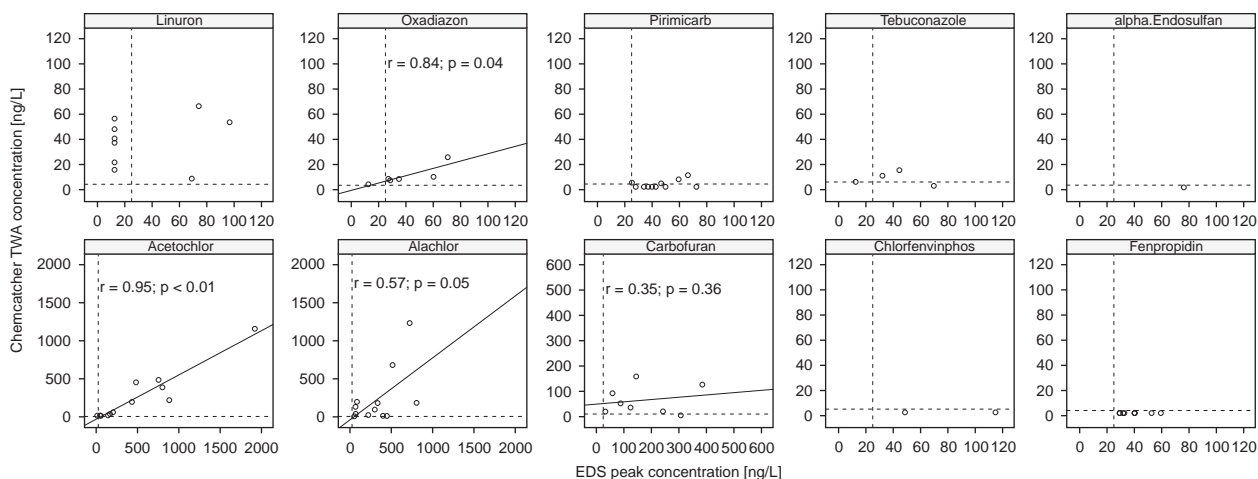


Fig. 4 – Relationship between the Chemcatcher[®] TWA concentrations and the EDS peak concentrations in 16 agricultural streams, for single compounds. Observations that were below LOQ for both sampling methods were excluded from analysis. Dashed lines indicate LOQ, r = Pearson's correlation coefficient. Regression lines are shown for >3 observations above LOQ for both methods.

Diuron (Alvarez et al., 2004). Concerning variation in TWA concentrations for replicate deployments of passive samplers, some studies reported similar findings (Stuer-Lauridsen, 2005; Alvarez et al., 2007), while another study with the Chemcatcher[®] found lower variability (RSD < 20%, $n = 2$), though the exposure time was 3-fold reduced compared to our study (Escher et al., 2006). Variation in the rate of uptake into the receiving phase may result from differences in biofouling and environmental conditions such as temperature or current velocity. Since environmental conditions are nearly identical within a single sampling point, we suggest that the variation in our study resulted from the high biofouling that was observed on the samplers after deployment (Greenwood et al., 2007). Therefore, new techniques are needed for polar passive samplers that help to reduce variability during field exposure, such as the PRC approach for non-polar compounds (Alvarez et al., 2007).

The derived TUs could reasonably well explain variation in the SPEAR index (Table 3). This suggests that variation in the composition of the invertebrate community could partly be attributed to pesticide stress and hence that the relative abundance of taxa classified as sensitive according to the SPEAR approach is reduced due to pesticides. A link between TWA concentrations and ecological effects was also found in two other studies (Leonard et al., 2000; Escher et al., 2006). Firstly, runoff-related endosulfan concentrations in passive samplers deployed in the Namoi river in Australia could be linked to the decline in invertebrate population densities (Leonard et al., 2000). Moreover, the Chemcatcher[®] was successfully employed to monitor herbicides and assess phytotoxicity in a small-scale field study in Australia (Escher et al., 2006). However, caution should be taken when relating TWA concentrations to effects on biota because no distinction can be made between a low-level chronic contamination and a short-term peak contamination on the basis of TWA concentrations. In a situation in which both chronic contamination and peak contamination are present, no link may be found between TWA concentrations and ecological effects.

Furthermore, the relationship between TWA concentrations and biotic metrics will most likely not hold in situations in which more than one peak event occurs during the exposure time. Nevertheless, passive samplers with a polar receiving phase may constitute a labour- and cost-efficient tool for field monitoring of polar organic toxicants when the exposure characteristics are known and episodic events are rare.

4.2. Comparison of the Chemcatcher[®] with the EDS

The Chemcatcher[®] passive sampler had a slightly lower number of total detections than the EDS (Table 3), but the concentrations were closely related ($r = 0.79$, $p < 0.01$, $n = 75$). Since the EDS sampled only one precipitation-driven runoff event (Fig. 1), the similarity of the TWA and EDS concentrations suggests that this event was the most relevant source of the pesticides sampled with the Chemcatcher[®]. Thus, our findings emphasize the relevance of field runoff as input path for pesticides in aquatic ecosystems and hence are in accordance with the results of previous studies in streams of Germany (Liess et al., 1999; Neumann et al., 2002). On average, the TWA concentrations were 4- to 5-fold lower than the EDS concentrations (Fig. 3). The concentrations determined with the EDS were assumed to represent peak concentrations during runoff (Liess et al., 2001; Schulz et al., 2001). Assuming that concentrations following runoff events drop to below 10% of the peak water concentration within 1–4 days (Richards and Baker, 1993; Leu et al., 2004), one would expect the TWA water concentrations to be in the range of $\frac{1}{12} - \frac{4}{12}$ of the EDS concentrations, based on an average exposure time of 12 days (Eq. (1)). Furthermore, this should be dependent on physicochemical properties of investigated pesticides and thus lead to significant differences between compounds. Indeed, we observed a significant difference in the relationship between TWA and peak concentrations for different compounds, though only for log-transformed concentrations. Furthermore, the slopes of the regression lines were different in separate linear regressions for the various

compounds (Fig. 4). Nevertheless, we are aware that more extensive data are needed to prove these differences between compounds.

4.3. Comparison of the Chemcatcher[®] with the suspended-particles sampler

Only five pesticides were detected on the suspended particles sampled with the SPS, and the total number of detections was significantly lower compared to the Chemcatcher[®] (Table 3). This may be explained by the polarity of the study compounds in view of the fact that the pesticides not detected had a $\log K_{ow} < 3.1$ except for oxadiazon (Table 1). Moreover, the smaller number of observations related to the SPS samples may be partly due to the LOQ, because it was a factor of 3–180 higher than the corresponding LOQs of the water samplers except for α -endosulfan, when assuming equilibrium partitioning between water and particulate phase (see LOQ calc., Table 1). The LOQ for the SPS could only be improved by stronger preconcentration of the eluate or by extracting an increased mass of suspended particles. Besides the fact that the amount of sample material from SPS was rather limited, both possibilities were hampered by the high magnitude of matrix coextraction masking the analyte peaks (Fig. 2). Thus, a more efficient SEC or solid phase extraction cleanup method for polar pesticides would be needed to achieve a lower LOQ (Dabrowska et al., 2003; Schäfer et al., 2007b).

Consequently, the particle-associated pesticide concentrations exhibited no significant correlation with the TWA concentrations or the EDS peak concentrations which refer to the dissolved water phase. This low similarity was also expressed by the proportion of cases ($\frac{18}{22}$) in which pesticides were found on suspended particles but not in samples collected by either the Chemcatcher[®] or the EDS. Similarly, no clear relationship between particle-associated contaminants and water concentrations was found in a 1-year monitoring study of 30 organic pesticides in six rivers in the UK (Long et al., 1998). Furthermore, high variability of the pesticide distribution between particulate and water phase was observed in tributaries of the Mississippi river (Pereira and Rostad, 1990) and in a field experiment on the release of six organic pesticides from a heavy clay soil during precipitation events (Brown et al., 1995). The contaminant distribution between particulate and water phase is influenced by environmental conditions, physicochemical properties and site-specific conditions that may explain the observed variation: (1) size of suspended particles, (2) composition and structure of organic matter in the particles (Zhou et al., 1995), (3) runoff-water flow rate (Gouy et al., 1999) and (4) lag time between pesticide application and runoff event. This variation in the pesticide partitioning between particulate and dissolved phase (Brown et al., 1995; Long et al., 1998) along with the high LOQ can explain why the results of the sampling with the SPS and the Chemcatcher[®] were very different.

Although the SPS samples indicated much higher pesticide stress in terms of STU compared to the TUs derived from the TWA and peak concentrations, no significant relationship could be established to the SPEAR index. By contrast, other

studies demonstrated significant linear relationships between STUs derived from bed sediments and the benthic community tolerance metrics (Wildhaber and Schmitt, 1998) or macroinvertebrate community composition (Friberg et al., 2003).

The differing results of our study most likely result from monitoring suspended particle concentrations instead of bed-sediment concentrations. Suspended particles in field runoff usually have much higher contaminant concentrations than bed sediments and are rarely in equilibrium with the water phase, rendering questionable the application of the STU approach (Liess et al., 1996; Long et al., 1998). In the present study, results from passive sampling and event-driven water sampling were more informative when used to explain variation in the invertebrate community. We propose that water concentrations are more likely to explain effects of episodic events with polar toxicants, whereas the effects of chronic exposure to hydrophobic compounds may be predicted from analysis of the sediment phase. However, this should be tested in future studies, and passive samplers in different configurations can be useful tools for such studies.

5. Conclusions

- The Chemcatcher[®] can be employed for continuous water sampling of polar organic toxicants for up to 14 days.
- The Chemcatcher[®] configured with a SDB-XC Empore[®] and without diffusion-limiting membrane represents a promising method for the monitoring of short-term exposure that conventional spot water sampling is likely to miss.
- Given the increasing attention that is paid to polar substances, a method similar to the performance reference compound concept is needed to account for variation in the passive sampling of polar compounds.
- Exposure assessment with the Chemcatcher[®] passive sampler yields results similar to water sampling but differs from suspended-particles sampling.
- In large-scale studies with frequently recurring pollution events, the Chemcatcher[®] is more labour- and cost-efficient than event-driven water sampling.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.watres.2008.01.023](https://doi.org/10.1016/j.watres.2008.01.023).

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