factor 1.02 (Table 3). Tebuconazole decreased most in sampling rate with a reduction of current velocity (factor 0.8).

Table 3: Sampling rates in the flow-through experiment

Pesticide	v = 0.135 m/s[b]		v = 0.4 m/s[b]	
	R_s[c] (L/day)	CV[a] (%)	R_s[c] (L/day)	CV[a] (%)
acetochlor	0.35	10.3	0.34	15.5
alachlor	0.32	16.5	0.31	11.7
atrazine	0.28	10	0.22	10
carbofuran	0.13	14.8	0.14	23.3
chlorfenvinphos	0.35	15.7	0.34	14.1
α-endosulfan	0.42	16.6	0.38	10.8
fenpropidin	0.3	19	0.27	17.8
hexazinone	0.26	24.2	0.21	15.9
linuron	0.12	21.5	0.13	17.8
oxadiazon	0.44	22.6	0.34	12.2
pirimicarb	0.38	20	0.29	11.4
tebuconazole	0.19	30.1	0.24	12.4

[a] coefficient of variation [b] flow velocity [c] sampling rate

Dependence of sampling rates on physicochemical properties

Although not significant, the sampling rates increased with the logarithmic octanol/water partition coefficients (log K_{ow}) of the compounds (Figure 3) ($p = 0.39$, $r^2 = 0{,}08$ for 0.135 m/s and $p = 0.2$, $r^2 = 0{,}16$ for 0.4m/s; $n = 12$). Removal of carbofuran and linuron slightly improved the relationship ($p = 0.34$, $r^2 = 0{,}11$ for 0.135 m/s and $p = 0.11$, $r^2 = 0{,}28$ for 0.4 m/s; $n = 10$). Sampling rates decreased with higher solubility (not shown) but the relationship was also not significant ($p = 0.74$ for 0.135 m/s; $p = 0.5$ for 0.4 m/s; $n = 12$).

Offload kinetics

For pirimicarb-D6 a nonlinear regression fit with Equation (4) could be obtained, but certain observations deviated strongly from the regression curve ($r^2 = 0.17$ for 0.135 m/s; $r^2 = 0.53$ for 0.4 m/s; $n = 8$). For chlorfenvinphos-D10 no acceptable regression fit was obtained for the low flow velocity ($r^2 = 0.03$ for 0.135 m/s; $r^2 = 0.43$ for 0.4 m/s; $n = 8$). The exchange rate constants k_e derived from the offload curves of pirimicarb-D6 and chlorfenvinphos-D10 were 0.02 d^{-1} (CV= 88%) and not evaluable for 0.135 m/s and 0.055 d^{-1} (CV= 38%) and 0.02 d^{-1}(CV= 48%) for 0.4 m/s, respectively. The estimation of

k_e from the uptake curves resulted in up to threefold higher values for pirimicarb-D6 (0.065 d^{-1} (CV= 80%) for 0.135 m/s and 0.09 d^{-1} (CV= 66%) for 0.4 m/s) and not reliable values for chlorfenvinphos-D10 (0.03 d^{-1} (CV= 287%) for 0.135 m/s and 0.01 d^{-1} (CV= 48%) for 0.4 m/s.)

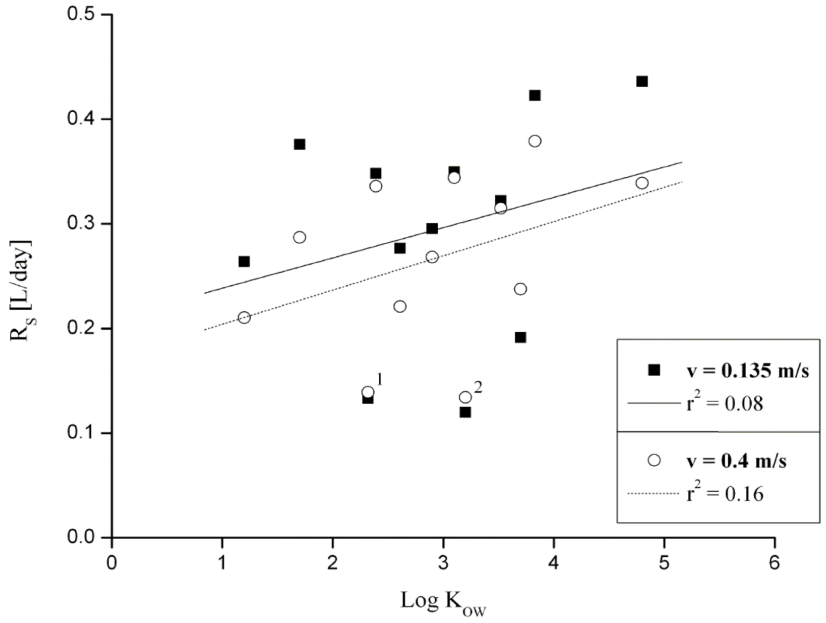

Figure 3: Relationship between sampling rates R_s and log $K_{ow.}$ Data taken from Table 1 and Table 3. 1 = carbofuran; 2 = linuron.

Discussion

Degradation of pesticides on the receiving phase

The decrease of recovery rates of linuron and carbofuran from the receiving phase over storage time indicated degradation on the SDB-XC disk. The main abiotic degradation pathway of carbofuran in water is base-catalysed hydrolysis to carbofuran-phenol, as described by Yu et al. (1974). Further products are 2,3-dihydro-2,2-dimethyl-benzofuran-4,7-diol, 3-ketocarbofuran (Yu et al., 1974) and 3-hydroxy-carbofuran-7-phenol (Chiron et al., 1996). It follows that under acidic and neutral condition, no significant hydrolysis is to be expected. Indeed, it was reported that in the dark at neutral pH, no degradation of carbofuran was observed during exposure times relevant to our experiment (Iesce et al., 2006, Munch and Frebis, 1992). By constrast, Iesce et al. (2006) reported a half-life of 3 hours for hydrolysis in the dark for carbofuran under alkaline

conditions (pH 9). Nevertheless, a study on the stability of carbofuran on a C_{18}-Empore disk reported up to 30% decrease in recoveries after 14 days of storage at temperatures up to 55°C (Cobb et al., 2006). These latter findings suggest that the Empore disk supports microbial activity and associated biodegradation of the compound. In our experiments we observed similar degradation rates, and in fact biofilms had developed on the disk to a visible extent after 14 to 21 days.

Degradation of linuron yielded 3,4-dichloroaniline as the major degradation product but was shown to be relatively persistent with a half-life of 945 days in water at pH values from 5 to 9 (Geißbuhler, 1975). However, Munch and Frebis (1992) reported a slight decrease in average recoveries (5%) when stored for 14 days at 4°C. On the SDB-XC Empore disks we observed a decrease of up to 49% recovery after 14 days. Again we assume that this is due to microbial degradation, as persistence in water was shown to be high.

As the Chemcatcher may be deployed up to 4 weeks, degradation of linuron and carbofuran is likely to occur in the field if the compounds are sampled from the stream. Hence, degradation should be taken into account when monitoring these two compounds, especially at high pH values (Bailey et al., 1996, Seiber et al., 1978).

Average concentrations during calibration experiments

During the calibration experiment several compounds exhibited high variation (Table 2). Average water concentrations in the first experiment (0.4 m/s) ranged from 64 to 168 ng/L, and variation was a little higher, up to 25% (n = 4). This was due to a two-fold increase of the analyte concentrations in the middle of the experiment (day 9) with a slight subsequent decrease. Since analyte concentrations were controlled only at 72-h intervals, we have no information about how long the concentrations were elevated. When presupposing a short time (< 12 h), the resulting average water concentrations would be reduced and therefore the computed sampling rates at 0.4 m/s were higher.

Overall the water concentrations were quite stable at 100 ng/L. The higher average concentrations at 0.4 m/s may have resulted from inaccuracies of the water pump resulting in lower water inflow while analyte input remained constant.

Uptake kinetics at different flow velocities

In our calibration experiment, we mostly observed lower sampling rates of analytes at faster flow velocities, with R_s values being 6.1 % smaller on an average. Under the investigated conditions with high and probably turbulent flow, no influence of the current velocity on the uptake kinetics was expected since the uptake should be governed solely by the sampler's resistance to mass transfer and not primarily by diffusion through the aqueous boundary layer. By contrast, this would be expected for non-polar compounds and was demonstrated by Vrana and Schüürmann (2002) for SPMDs for very slow flow (0.0006 m/s, 0.0028 m/s). However, they found flow-independent sampling rates for a hydrophobic compound (log K_{ow} = 5.5) when current velocities increased to 0.0114 m/s, and slightly decreasing R_s values for lindane (log K_{ow} = 3.8).

The sampling rates in our study exhibited significant differences when compared in pairs for the two current velocities (paired sample t-test, t = -2.2152, p = 0.049; n = 12). However, after removal of the elevated water concentration at 0.4 m/s, the R_s values would not be significantly different (paired-sample t-test, t = 1.2283, p = 0.2450; n = 12). Hence we suggest that the differences between the sampling rates can be attributed to variability in the analyte concentrations in water between the experiments rather than to differences in uptake kinetics. The influence of flow velocity on the sampling rate seems to play a minor role for hydrophilic substances, and other calibrations were run with stirred water only (Alvarez et al., 2007). Nevertheless more studies are needed regarding the influence of current velocity on the sampling rate, as this is a very important environmental variable in field deployments.

Comparison of sampling rates

An overview of our sampling rates and those of previous studies is given in Table 4. The sampling rates of Stephens et al. (2005) for hexazinone and atrazine were two-fold and four-fold higher compared to our values (Table 4). This may be due to a higher temperature in their experiment as pointed out by Vrana et al. (2006a, 2007) for other compounds. Furthermore, they used different receiving phases (SDB-RPS and C_{18} Empore disks). The SDB-RPS phase contains additional sulfonic acid functional groups to improve mass transfer compared to the SCB-XC disk, which can explain the higher sampling rates. However, higher sampling rates resulted in a shorter linear uptake phase of the sampler. Thus the advantage of employing a SDB-XC Empore disk would be a

longer exposure period until equilibrium is reached. When a diffusion-limiting membrane is employed, further prolongation of this period is possible, but the sampling rates of the SDB-XC disks for atrazine decreased by a factor of 10 (Tran et al., 2007). This is in accordance with a study of Kingston et al. (2000) where the use of a membrane resulted in a five-fold decrease of the accumulated mass of atrazine on a C_{18} disk.

The R_S value of endosulfan was 0.379 L/day at a flow velocity of 0.4 m/s in our experiment. Vrana et al. (2006a) found sampling rates between 0.06 to 0.15 L/day for endosulfan with a C_{18} Empore disk as receiving phase, covered with a LDPE membrane and exposed to flow velocities of 0, 0.4 and 0.7 m/s. In recent studies on polar organic chemical integrative sampler disks (POCIS), sampling rates of several pesticides were similar to those of our study and ranged from 0.026 L/day for Carbofuran to 0.3 L/day for Pirimicarb (Alvarez et al., 2007). Our results demonstrate that the Chemcatcher can be adapted according to the desired time of exposure.

Table 4: Comparison of our sampling rates and previous studies

Setup Conditions				**Pesticides calibrated in several studies with R_S values (L/day)**			
Receiving phase	Membrane	T (°C)	v (m/s)	atrazine	hexazinone	endosulfan	Reference
SDB-XC	PES[a]	23	0.004	0.023			Tran et al. (2007)
C18	-	22	0.14	1.4	0.74		Stephens et al. (2005)
SDB-RPS	-	22	0.14	1.2	0.6		Stephens et al. (2005)
SDB-XC	-	14	0.135	0.28	0.26		This study
SDB-XC	-	14	0.4			0.38	This study
C18	LDPE[b]	11	0.4			0.08	Vrana et al. (2005)

[a] PES – polyethersulfone [b] LDPE – low density polyethylene

Relationship between sampling rates and physicochemical properties

Vrana et al. (2006a) demonstrated a strong linear relationship between log K_{ow} and the sampling rate for non-polar substances (log K_{ow} = 3.5 - 7). For more polar pesticides (log K_{ow} = 1.2 – 2.85) Stephens et al. (2005) suggested an increasing sampler-water equilibrium-partitioning coefficient log K_{sw}, which is proportional to the sampling rate, with increasing log K_{ow} (Stephens et al., 2005). In our experiment, no significant relationship was found between log K_{ow} and sampling rate (Figure 3). The low correlation between the sampling rate and log K_{ow} in our study may be explained by the uptake mechanism to the receiving phase, as this is adsorption for the SDB-XC disk in contrast

to partitioning for C_{18} disks (Mills et al., 2007).

Offload kinetics

PRCs present a relevant method of coping with between-site variation of environmental variables and biofouling that may result in differences in the analyte uptake during field deployment (Huckins et al., 2002). Although we did not discover a significant effect of flow velocity on the sampling rate, PRCs for polar pesticides would be useful to account for in situ variation of other environmental factors such as biofouling or water temperature during field deployment. The application of PRCs relies on isotropic behaviour of uptake and release kinetics (Gorecki and Namiesnik, 2002). Several studies demonstrated isotropic kinetics for hydrophobic compounds and different receiving phases (Vrana et al., 2006a, Vrana et al., 2007, Vrana et al., 2006b). In studies on PRCs for polar compounds, isotropic behaviour was found for triclopyr (log K_{ow} = -0.45) for the SDB-XC Empore disk (Tran et al., 2007) and for desisopropylatrazine (log K_{ow} = 1.15) for the POCIS (Mazzella et al., 2007). Both studies employed a polyethersulfone diffusion-limiting membrane. In our study, the nonlinear regression fit of the offload curve was bad compared to these studies. Furthermore, we did not observe a clear elimination of the PRCs from the receiving phase for low-flow conditions (Figure 4a and 4b). Due to the high variation in exchange rate constants, the isotropy of uptake and offload kinetics could not be confirmed reliably for the uncovered receiving phase.

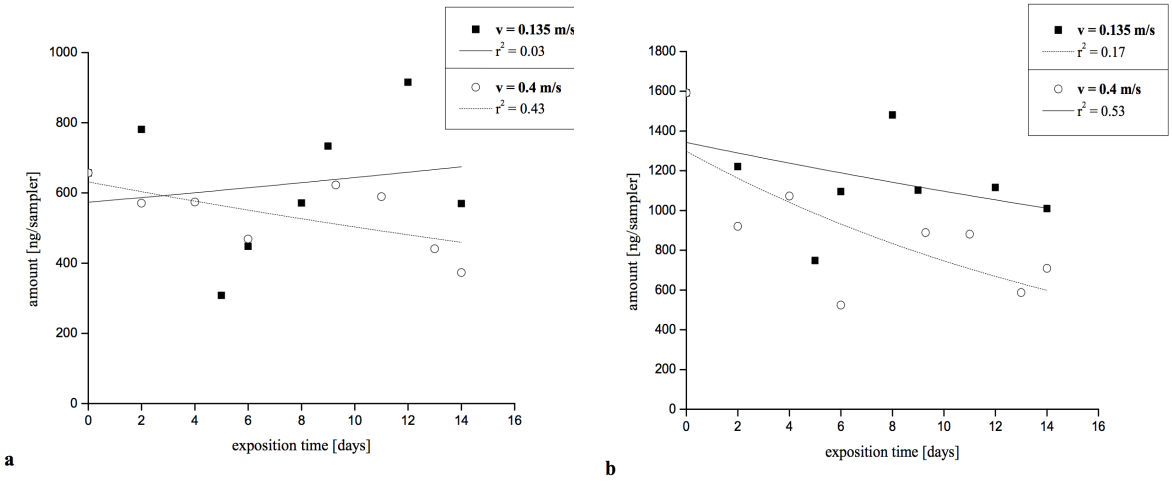

Figure 4: Nonlinear regression fit for offload curves of the performance reference compounds chlorfenvinphos-D10 (4a) and pirimicarb-D6 (4b) from the SDB-XC receiving phase. v = flow velocity.

A possible explanation for the differences to previous studies is that the PRCs are not loaded homogeneously over the thickness of the receiving phase. This may result in high variation when no diffusion-limiting membrane is used. Another explanation was given by Mills et al. (2007), who described the use of PRCs with polar receiving phases as problematic because their accumulation is rather determined by adsorption than by partitioning. Thus, uptake and offload kinetics could not be governed by the same mass transfer law. However, the use of a diffusion-limiting membrane may overcome this problem as demonstrated by Tran et al. (2007) and Mazzella et al. (2007), with being the limiting step of the mass transfer between sampler and surrounding medium. Furthermore, the use of a diffusion-limiting membrane may reduce biofouling due to a lower surface area compared to the Empore disk. Nevertheless, the membrane would limit the sampling rate, and brief fluctuations of analyte concentration during exposure may be missed.

Conclusions

The Chemcatcher passive sampler with SDB-XC Empore disc as receiving phase is suitable for the use in time-integrative water monitoring of polar compounds, and we provide sampling rates for future field studies. Flow velocity is of minor importance in field deployments for rates between 0.15 and 0.4 m/s, as this variable seems to not affect the sampling rates. By contrast, degradation on the receiving phase is relevant and needs to be accounted for, because the derived TWA concentrations would underestimate real exposure otherwise. Furthermore, new techniques are needed to account for between-site differences in environmental conditions, as PRCs may not be applicable for polar receiving phases without membranes.

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Kapitel 4: 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 µg/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 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.

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 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® to 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; Liess et al., 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; Schäfer et al., 2007b). The 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.

Materials and methods

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 (27510 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).

Preparation, deployment and extraction of the passive sampler

The Chemcatcher® passive sampling device (University Portsmouth, UK; commercially available at Alcontrol AB, Linkoping, Sweden) was employed for continuous water monitoring as described by Kingston et al. (2000). The Chemcatcher® consists of a

polytetrafluorethylene (PTFE) sampler body and for the purpose of this study was equipped with SDB-XC Empore® disks (3M, Neuss, Germany) as 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 hours). 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 9-11th of May for 10 to 13 days (Figure 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 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.

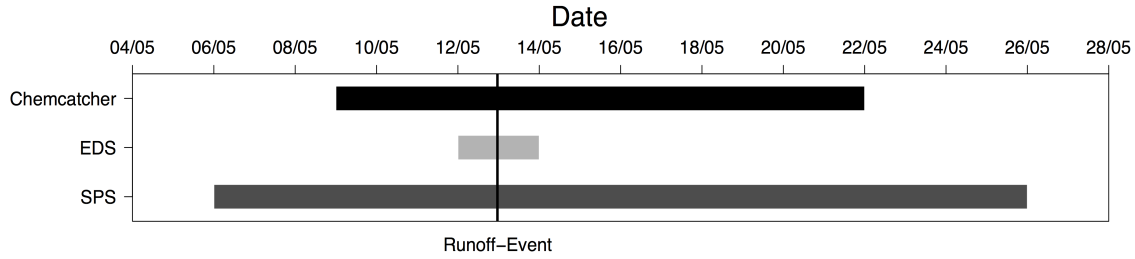

Figure 1: Sampling scheme for the three monitoring methods in 16 French streams. "Runoff-Event" indicates a heavy precipitation event (> 10 mm/day).

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

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 Figure 2.

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	chloro-acetamide	2.39	2.32	5.1	25	12.5	0.26	9000
Alachlor	H	chloro-acetamide	3.52	2.28	5.4	25	12.5	0.24	10000
α-Endosulfan	I	organo-chlorine	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 10g 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: $\text{LOQ calc.} = \text{LOQ EDS} * K_{OC} * f_{OC}$ 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

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/d (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 Equation (1).

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

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