(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).

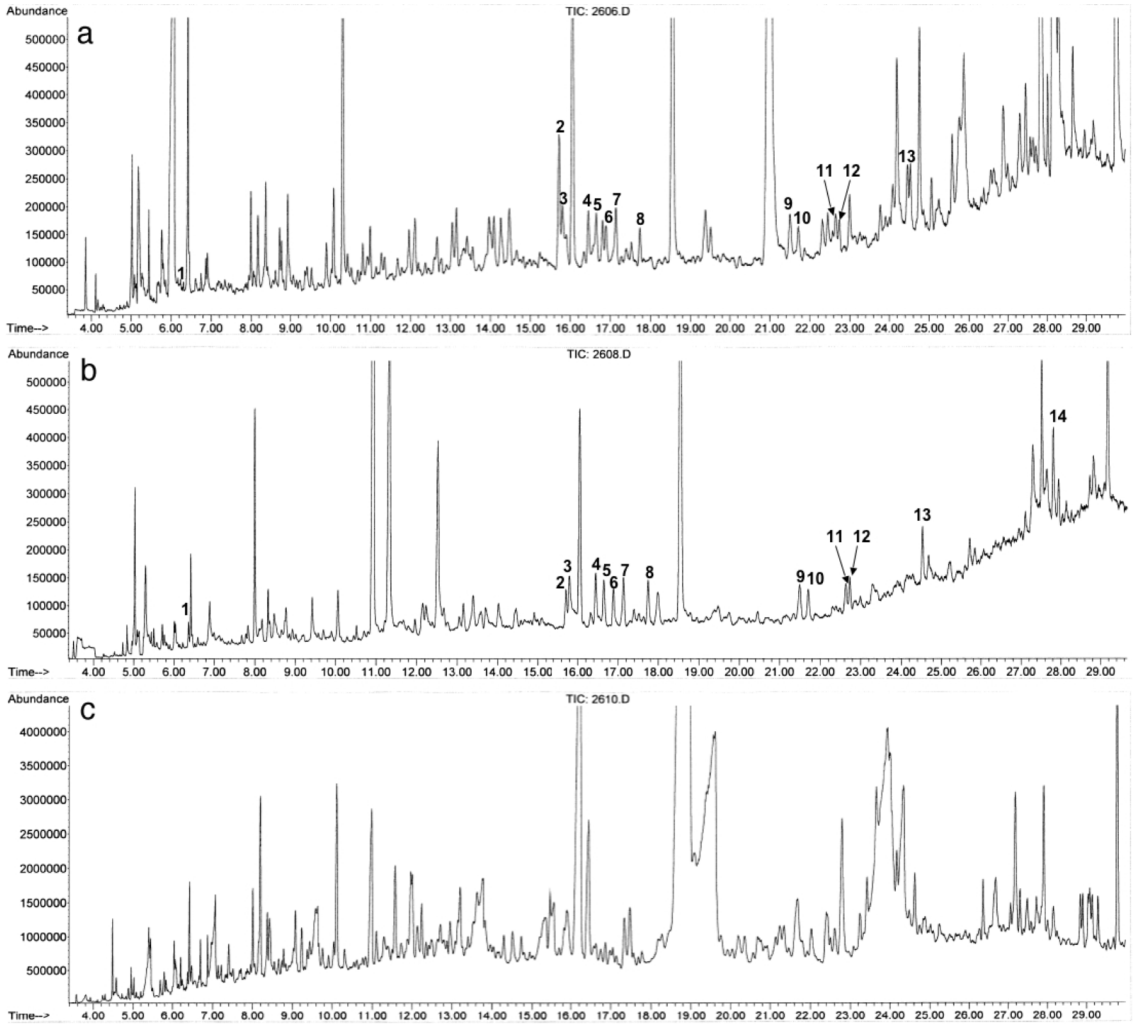

Figure 2: Typical total-ion chromatograms for (a) the event-driven water sampler (EDS), (b) the Chemcatcher®, and (c) the suspended-particle sampler (SPS). The samples were spiked with 1 µg/L (SPS 100 µg/kg) of pesticide standards. Deuterated internal standards were only used for comparison of the EDS 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

Description of the event-driven water sampler (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/ 24 h) the filled sample bottles were retrieved and water samples were solid-phase-extracted using

6 ml Chromabond HR-P columns containing 500 mg of polystyrene-divinylbenzene (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 12th and 13th of May (Figure 1). The TUs of this method were taken from Schäfer *et al.* (2007a).

Description of the suspended-particle sampler (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 two-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 were extracted using 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 µl and subsequently, 50 µl TPP were added as IS. To obtain comparable data sets, we used the results of the sampling period between 6th to 23-26th of May for this method (Figure 1). A maximum sediment toxic unit was computed from the suspended particle concentrations as described in Schäfer *et al.* (2007b). Log-transformed sediment toxic units are referred to as STU.

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 the 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:

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

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. 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).

Results

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 fenpropidine. Both chloroacetamide herbicides - acetochlor and alachlor - were detected most frequently above the LOQ and had the highest TWA concentrations, reaching up to 1 µg/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 relative range (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 *Daphnia magna*, to -5 (Table 2). The TU-values explained reasonably well 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.

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).

Table 2: Time-weighted average concentrations in ng/L (± 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 (± 148%)	12 (± 99%)	bq	16 (± 94%)	4 (±72%)	5 (± 86%)	bq	-2.6	-2.5	-5.0
7	37	132	92	57	bq	8	bq	-3.5	-2.1	-5.0
8	454 (± 102%)	681 (± 99%)	159 (± 27%)	41 (± 116%)	9 (± 103%)	bq	bq	-2.4	-0.8	0.9
9	486 (± 29%)	1233 (± 14%)	52 (± 22%)	22 (± 25%)	bq	bq	15 (± 10%)	-2.9	-2.6	-2.0
10	388 (± 55%)	182 (± 44%)	20 (± 13%)	66 (± 48%)	26 (± 95%)	6 (± 26%)	11 (± 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 (± 120%)	24 (± 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 Equation 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).

The concentrations determined with the EDS were in general a factor of 4 to 5 higher than the Chemcatchers' TWA concentrations (Figure 3). The linear regression model, encompassing EDS' 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, $p < 0.05$) (Figure 4).

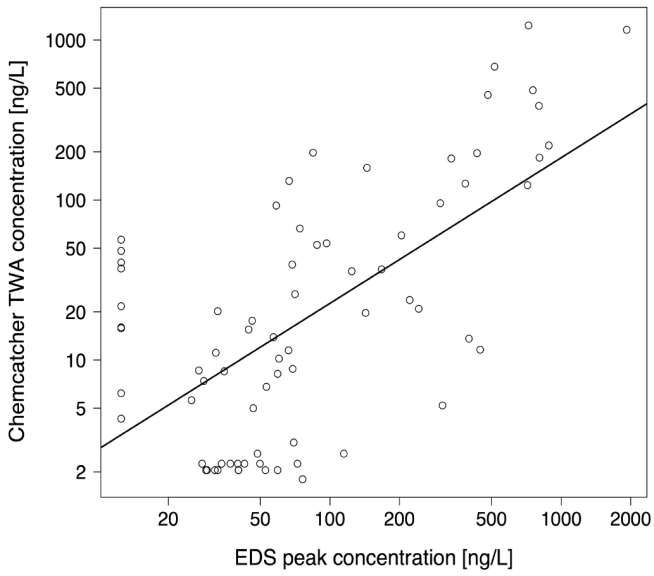

Figure 3: Relationship between the Chemcatcher® TWA concentrations and the EDS peak concentrations in 16 agricultural streams, on a double logarithmic scale. Observations that were below LOQ for both sampling methods were excluded from analysis. Model parameters: $r^2 = 0.4$, $p < 0.01$, $n = 75$. Model parameters for non log-transformed concentration: $r^2 = 0.62$, $p < 0.01$, $n = 75$.

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).

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 *Daphnia magna*. For water concentrations, the TUs peaked at -0.42, equivalent to 1/2.5 the LC50 value for *Daphnia magna* (Table 2). The TUs of the two water sampling methods were very similar, indicated by a *r* of 0.94 ($p < 0.01$, $n = 16$). The SPEAR index was reasonably well explained by the toxic units of the EDS and the Chemcatcher® whereas no significant linear relationship was observed between STUs and SPEAR (Table 3).

Discussion

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 fenpropidine, 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 fenpropidine, 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 µg/L were reported for 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 (relative standard deviation (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).

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[b]
Chemcatcher®	7	54	$r^2 = 0.50$ ($p < 0.01$)
EDS	10	66	$r^2 = 0.38$ ($p = 0.01$)
SPS	5	22[a]	$r^2 = 0.01$ ($p > 0.05$)

[a] Significantly lower than the total detections by the other methods in multiple comparison tests (χ^2-test with Bonferroni correction, $p < 0.05$). [b] Linear regression with the respective TUs/STUs as explanatory variable and SPEAR as response variable.

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.