

Figure 4: Relationship between the Chemcatcher<sup>®</sup> 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.

*Comparison of the Chemcatcher<sup>®</sup> with the event-driven water sampler*

The Chemcatcher<sup>®</sup> 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 (Figure 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<sup>®</sup>. 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 (Figure 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 to 4 days (Richards and Baker, 1993; Leu et al., 2004), one would expect the TWA water concentrations to be in the range of 1/12 to 4/12 of the EDS concentrations, based on an average exposure time of 12 days (Equation 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 (Figure 4). Nevertheless, we are aware that more extensive data are needed to prove these differences between compounds.

*Comparison of the Chemcatcher<sup>®</sup> 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<sup>®</sup> (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 to 180 higher than the corresponding LOQs of the water samplers except for  $\alpha$ -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 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 (Figure 2). Thus a more efficient size exclusion chromatography 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 (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.

## Conclusions

- The Chemcatcher<sup>®</sup> can be employed for continuous water sampling of polar organic toxicants for up to 14 days.
- The Chemcatcher<sup>®</sup> configured with a SDB-XC Empore<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> is more labour- and cost-efficient than event-driven water sampling.

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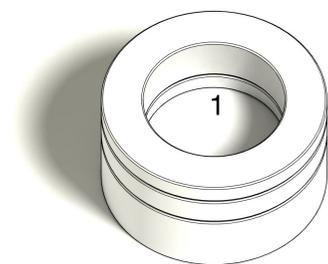
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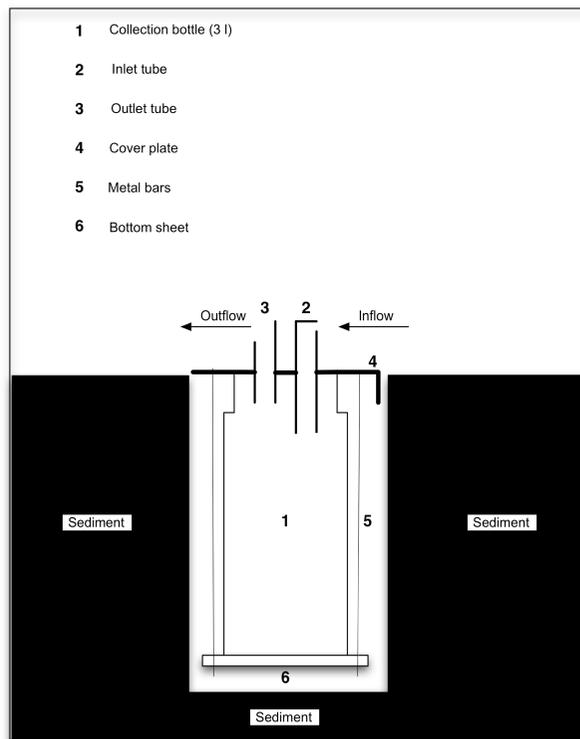
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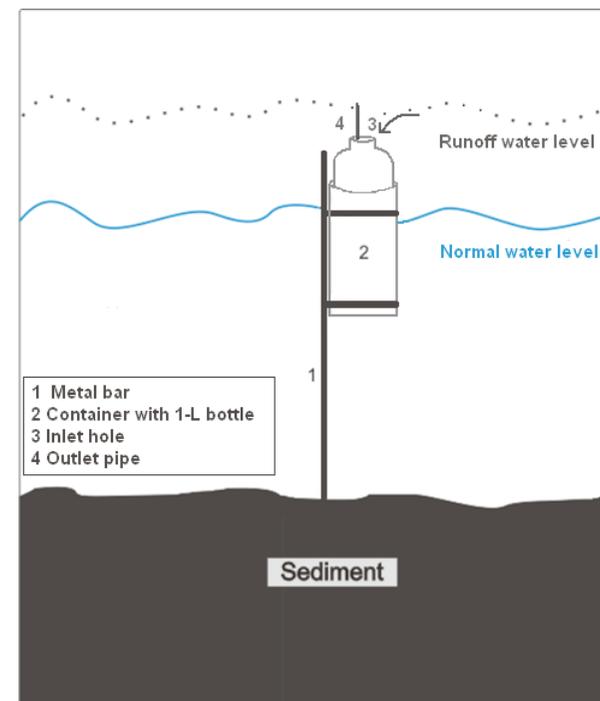
## Supplementary material



Chemcatcher<sup>®</sup> passive sampler with SDB-XC receiving phase (1). The receiving phase was directed towards the stream bottom during deployment.



Suspended-particle sampler (SPS)



Event-driven water sampler (EDS)



# **Kapitel 5: Effects of pesticides on community structure and ecosystem functions in agricultural streams of three biogeographical regions in Europe**

Ralf Bernhard Schäfer<sup>1,2</sup>, Thierry Caquet<sup>3</sup>, Katri Siimes<sup>4</sup>, Ralf Mueller<sup>5</sup>, Laurent Lagadic<sup>3</sup> & Matthias Liess<sup>1</sup>. 2007. *Science of the Total Environment* 382: 272-285

<sup>1</sup>UFZ - Helmholtz Centre for Environmental Research, Dept. System Ecotoxicology, Permoser Straße 15, 04318 Leipzig, Germany

<sup>2</sup>University Lüneburg, Institute for Ecology and Environmental Chemistry, Scharnhorststraße 1, 21335 Lüneburg, Germany

<sup>3</sup>UMR 985 INRA–Agrocampus, Ecobiologie et Qualité des Hydrosystèmes Continentaux (EQHC), Equipe Ecotoxicologie et Qualité des Milieux Aquatiques, 65 rue de Saint Briec, 35042 Rennes, France

<sup>4</sup>Finnish Environment Institute (SYKE), Research Programme for Contaminants, Mechelininkatu 34a, 00241 Helsinki, Finland

<sup>5</sup>EWE AG, Department UT – Laboratory for Environmental Analytics, Bürgerparkstraße 11, 49661 Cloppenburg, Germany

Correspondence author: [Ralf.Schaefer@ufz.de](mailto:Ralf.Schaefer@ufz.de)

## **Abstract**

There is a paucity of large-scale field investigations on the effects of organic toxicants on stream macroinvertebrate community structure and ecosystem functions. We investigated a total of 29 streams in two study areas of France and Finland for pesticide exposure, invertebrates and leaf litter breakdown. To link pesticide exposure and community composition we applied the trait-based Species At Risk (SPEAR) indicator system.

In the French region, pesticide stress was associated with a decrease in the relative abundance and number of sensitive species in the communities. The presence of undisturbed upstream reaches partly compensated the effects of pesticide contamination. Functional effects of pesticides were identified by a 2.5-fold reduction of the leaf litter breakdown rate that was closely correlated with the structural changes in the contaminated streams. No effects of pesticides were observed in Finnish streams since contamination with pesticides was very low.

In a follow-up analysis, the SPEAR approach successfully discriminated between reference and contaminated sites across different biogeographical regions, also including

results of a previous field study in North Germany. Furthermore, change of the community structure was detectable at a concentration range as low as 1/100 to 1/1000 the acute 48h-LC50 of *Daphnia magna*. Our findings demonstrate that pesticides may influence the structure and function of lotic ecosystems and that the SPEAR approach can be used as a powerful tool in biomonitoring over large spatial scales.

## Introduction

Pesticides represent a relevant stressor for many aquatic and terrestrial species (Liess et al., 2005b). They have been shown to potentially affect all groups of organisms in aquatic ecosystems: e.g. microorganisms (DeLorenzo et al., 2001), invertebrates (Castillo et al., 2006), plants (Frankart et al., 2003) and fish (Grande et al., 1994).

Although some field studies demonstrated effects of heavy metals on the aquatic community structure at the regional scale, there is a paucity of such investigations for organic toxicants, encompassing more than one stream or river (Clements et al., 2000; Beasley et al., 2003; Maret et al., 2003). Furthermore, the effects of current-use pesticides on important stream ecosystem functions such as leaf litter breakdown (Wallace et al., 1997) are still largely unknown.

The establishment of a causal relationship between a stressor and effects can be hampered by natural variability, as every sampling site exhibits a unique combination of environmental variables and species (Liess et al., 2005b). In addition, confounding factors like the occurrence of other anthropogenic or natural stressors can mask the effects of a particular stressor. The use of species traits, such as generation time or dispersal capacity, represents an interesting approach towards encompassing both natural variability and confounding factors (Statzner et al., 2005). As most stressors or environmental gradients affect only certain trait modalities, called response traits, trait-based approaches may be used to identify the effects of a specific stressor e.g. pesticides. At the community level, the relative abundance or number of species with certain trait modalities would probably decrease thus making it possible to interpret and/or predict community change (Statzner et al., 2005). Recently, Liess and von der Ohe (2005) developed a trait-based concept with which to distinguish pesticide effects on freshwater macroinvertebrates from the influence of other environmental variables. This concept, called Species At Risk (SPEAR), classifies macroinvertebrates according to their vulnerability towards pesticides into

sensitive species (SPEAR) and tolerant species (SPEnotAR), as evaluated by selected ecological and physiological traits. The authors successfully employed this approach in a field study on 20 streams in North Germany, where the relative abundance of SPEAR in a community declined with increasing pesticide stress. Furthermore, pesticide stress was the most important explanatory variable for different community-based SPEAR-endpoints (Liess et al., 2005a). In another study, Schriever et al. (2007) demonstrated that the highest correlation between the fraction of sensitive species and various environmental parameters was obtained for a modelled indicator of pesticide exposure, called runoff potential.

In the present study we aimed at investigating if (1) the use of the SPEAR concept in biomonitoring may be extended beyond North Germany to different biogeographical regions (Illies, 1978) and (2) pesticides have effects not only on the structure but also on the functioning of aquatic ecosystems. Therefore, we conducted field investigations in two regions of France and Finland in which the macroinvertebrate communities, leaf litter breakdown, pesticides and physico-chemical characteristics of 29 streams were monitored during the period of pesticide application. Considering the differences in agricultural practices and especially pesticide use between these countries, we were also able to examine whether the effects of pesticides on non-target organisms are dependent on usage patterns or if the invertebrate communities adapt accordingly. To our knowledge, this is the first study that comparatively investigates pesticide effects in different biogeographical regions.

To further evaluate the performance of the SPEAR approach in large-scale biomonitoring we analyzed its ability to discriminate reference and contaminated sites across different biogeographical regions, also including the sites of the previous field study in North Germany (Liess et al., 2005a).

## **Methods**

### *Study area and sampling schedule*

France and Finland were selected as study countries because they belong to different biogeographical regions (Illies, 1978) and exhibit contrasting pesticide use with an average of approximately 6 and 0.8 kg annually applied active ingredient per hectare,

respectively (EUROSTAT, 2002). This difference partly stems from the lower prevalence of pests in Finland since the northward dispersal of many pests is averted by the colder climate. In France, Brittany in the northwest was chosen as study area because the local authorities reported frequent regional and temporal contamination of streams with pesticides from 2002 to 2004 (DIREN, 2005). A total of 16 sampling sites in first- to third-order lowland streams (Strahler, 1957) were selected which were expected to exhibit a gradient in pesticide contamination based upon the analysis of local authorities' monitoring data (Regional Agency for Agriculture and Forestry (DRAF) Bretagne, personal communication). Since Finnish agriculture is mainly localized in the southern part of the country, this region was chosen for the specification of sampling sites. 13 sites were selected in first- to third-order lowland streams covering different areas of South Finland.

All streams in the two regions of France and Finland were selected to match the physical properties of those sampled during a previous field study in North Germany (Liess et al., 2005a): no drying up in summer; no dredging in the present or past year; presence of adjacent fields with vegetable, corn or oil-seed crops; average stream current velocity ranging between 0.1 and 0.5 m/s; maximum stream depth of 0.8 m. Furthermore, the sites were checked in field survey and with maps (France: IGN 1:25,000 maps, Finland: Maanmittauslaitos 1:50,000 maps) to have no waste-water treatment plants, industrial facilities or mining drainage upstream. Thus, pollution other than from agricultural sources was unlikely. The location of all sampling sites is displayed in Figure 1.

The sites were sampled before (14-19 April 2005 in France, 3-9 July 2005 in Finland) and during (19-26 May 2005 in France, 1-6 August 2005 in Finland) the estimated period of maximum pesticide contamination, according to the monitoring data from local authorities (France: DRAF Bretagne, Finland: Finnish Environment Institute (SYKE), personal communication). However, the timing of pesticide application varies and the sites may therefore have received pesticide input before the initiation of sampling. This holds especially for France, where strong rain was recorded three days before the first sampling date, possibly leading to pesticide runoff. If stated below, we also included in the analysis the results of the study in the German region for April and May, averaged for the 3 years of study (Liess et al., 2005a). We are aware that the results of non-randomly chosen, single regions cannot be extrapolated to the country level. However, for the ease of reading we refer to the respective region with the countries' name throughout this paper.

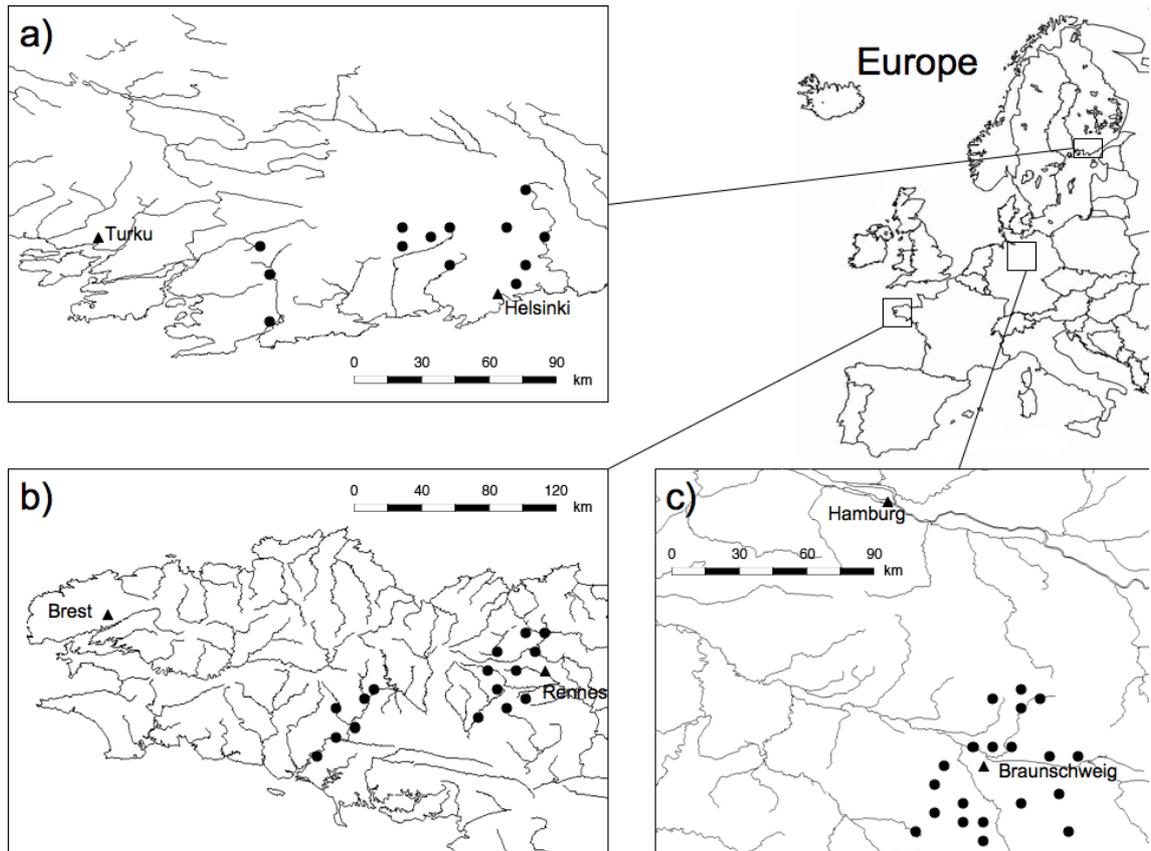


Figure 1: Map of sampling sites and large rivers in Finland (a), France (b) and Germany (c). Sampling streams are not displayed due to scale. Regional maps were created using ESRI World Basemap Data and the European map was created with R (packages: maps and mapdata).

#### *Physico-chemical and geographical parameters*

Concentrations of oxygen, ammonium, nitrite, nitrate and orthophosphate in the stream water as well as temperature, pH and stream current velocity were measured as described in Liess and von der Ohe (2005). Water conductivity was determined on site with a device Multi 340i device of WTW (Weilheim, Germany). Total water hardness was measured in the field with an Aquamerck test (precision: 1°dH; Merck, Darmstadt, Germany). Suspended matter was collected in suspended-matter samplers (Liess et al., 1996), measured biweekly and converted into a volume (ml) per week. In-stream structure, depth, width, tailing and buffer strip width were investigated in a 50-m reach upstream and downstream from the sampling site.

Previous studies demonstrated that the presence of forested upstream stretches that are undisturbed in terms of agricultural activities positively influenced downstream habitat quality and partly compensated for the effects of pesticides (Liess et al., 2005a; Schriever et al., 2007). Therefore we inspected the French and Finnish streams upstream of each

sampling site in field survey or with maps (France: IGN 1:25,000 maps, Finland: Maanmittauslaitos 1:50,000 maps) for the presence of riparian forests. If double-sided riparian forests at least 100 m in length were present in the 3-km reach upstream of a sampling site, we categorized it as having an undisturbed upstream reach. Modification of these criteria such as different upstream distances (2 or 4 km) or the presence of single-sided instead of double-sided forest stretches had no appreciable effects on the results of the present study. An overview of the stream characteristics, including the sites previously investigated in Germany (Liess et al., 2005a) is given in Table 1.

### *Pesticide monitoring and chemical analysis*

The substances for the screening programmes in France and Finland were selected by (1) identifying potential compounds based upon the analysis of previous regulatory monitoring programmes (France: DRAF Bretagne, Finland: Finnish Environment Institute (SYKE), personal communication) and (2) ranking them according to their toxicity, indicated by the 48-h acute median lethal concentration (LC50) for *Daphnia magna* as given in Tomlin (2001). The 10 most toxic pesticides included in the respective screening program were mainly non-polar ( $\log K_{ow} > 4$ ) for Finland and polar to semi-polar ( $\log K_{ow} < 4$ ) for France (Table 2). The sampling methods were arranged to catch runoff-induced exposure because this is a major input path for pesticides in small streams (Neumann et al., 2002). They were locally adapted due to differences in polarity and expected concentration levels of the compounds.

In France, runoff-triggered water samplers (Liess et al., 1999b) were deployed and retrieved after heavy rain events ( $> 10$  mm precipitation per day). The water samples were subsequently solid-phase-extracted using 6 ml Chromabond HR-P columns (Macherey-Nagel, Düren, Germany). Analytes trapped on the columns were extracted with 10 ml of 1:1 acetonitrile-ethylacetate and the extract gently evaporated under nitrogen to 0.3 ml. Residue analysis was conducted on an Agilent 6890N (Agilent Technologies Germany, Boeblingen, Germany) gas chromatograph (GC) linked to an Agilent 5973 mass selective detector (MSD).

In Finland, continuous water passive sampling was performed with low-density polyethylene (LDPE) strips (Booij et al., 2003), which were deployed in each stream at the beginning of the study and exposed for 28 days. LDPE strips were extracted by soaking in 500 ml n-hexane for 48 h.

Table 1: Descriptive statistics of environmental parameters at the study sites in France, Finland and Germany.

Parameter	unit	France <sup>5</sup>					Finland <sup>5</sup>					Germany <sup>6</sup>				
		Mean	SD	% SD	Min.	Max.	Mean	SD	% SD	Min.	Max.	Mean	SD	% SD	Min.	Max.
Water temperature <sup>1</sup>	°C	12.58	1.21	9.65	10.55	15.40	17.74	1.89	10.64	13.30	20.10	13.30	3.00	22.56	3.50	19.50
pH <sup>1</sup>		6.94	0.30	4.34	6.59	7.60	6.97	0.34	4.93	6.45	7.65	7.90	0.34	4.30	6.80	8.60
Ammonium	mg/L	0.07	0.10	143.85	0.00	0.38	0.11	0.28	261.77	0.00	1.00	0.07	0.21	300.00	0	1.75
Nitrite	mg/L	0.06	0.05	78.77	0.00	0.13	0.05	0.14	273.62	0.00	0.50	0.15	0.13	86.67	0.01	0.80
Nitrate	mg/L	15.63	7.83	50.09	0.00	27.50	0.00	0.00	0.00	0.00	0.00	3.40	9.20	270.59	0.50	47.5
Orthophosphate	mg/L	1.01	0.91	90.75	0.13	3.50	0.20	0.23	114.53	0.00	0.88	0.19	0.13	68.42	0.00	0.60
Hardness <sup>1</sup>	°dH	6.28	2.13	33.89	3.00	9.00	4.54	0.97	21.32	3.00	6.50	not measured				
Conductivity	µS/cm	183.23	87.72	47.87	86.00	387.00	160.54	58.96	36.72	76.00	277.00	not measured				
Oxygen	mg/L	10.63	0.98	9.21	8.80	12.10	10.21	2.55	24.99	5.86	15.80	10.20	2.20	21.57	3.40	13.80
Current velocity	m/s	0.31	0.14	46.32	0.10	0.73	0.27	0.10	37.00	0.15	0.50	0.17	0.09	52.94	0.02	0.50
Depth	m	0.27	0.11	40.27	0.15	0.60	0.27	0.11	43.09	0.10	0.40	0.16	0.10	62.50	0.04	0.60
Width	m	2.61	1.04	39.73	1.00	4.50	2.12	0.77	36.30	1.00	3.00	1.30	0.44	33.85	0.50	2.50
Tailing	%	48.28	18.11	37.52	17.50	80.00	63.08	22.78	36.11	30.00	90.00	not measured				
Twigs	%	6.63	2.63	39.70	3.50	12.50	8.46	4.27	50.51	0.00	15.00	not measured				
Free substrate <sup>2</sup>	%	64.09	15.84	24.71	30.00	78.00	72.31	14.52	20.08	45.00	85.00	not measured				
Allochthonous leafs	%	8.28	3.38	40.83	5.00	15.00	2.69	6.96	258.40	0.00	25.00	20.00	28.0	140.00	0.00	100.00
Submersed plants <sup>2</sup>	%	14.75	16.36	110.88	2.50	57.50	5.00	8.16	163.30	0.00	30.00	8.00	11.0	137.50	0.00	50.00
Emersed plants	%	4.13	4.15	100.69	0.00	15.00	9.23	9.97	107.99	0.00	30.00	5.00	9.00	180.00	0.00	65.00
Filamentous alga	%	2.13	2.96	139.20	0.00	10.00	2.31	2.59	112.42	0.00	5.00	1.00	4.00	400.00	0.00	25.00
Boulder (> 20 cm)	%	6.25	8.06	129.00	0.00	35.00	3.08	3.25	105.70	0.00	10.00	0.00	0.00	0.00	0.00	0.00
Cobble (5-20 cm)	%	7.50	6.83	91.08	0.00	20.00	13.46	12.81	95.16	5.00	50.00	2.00	7.00	350.00	0.00	30.00
Gravel (1-5 cm) <sup>4</sup>	%	15.31	10.24	66.89	5.00	30.00	13.46	8.75	65.02	0.00	30.00	5.00	10.0	200.00	0.00	40.00
Grit (0,1-1 cm)	%	21.25	9.40	44.23	10.00	50.00	16.92	10.52	62.14	5.00	30.00	other classification				
Sand (0,01-0,1 cm)	%	27.19	13.54	49.79	10.00	55.00	28.46	13.75	48.32	10.00	60.00	24.00	37.0	154.17	0.00	100.00
Clay and silt (< 0,01) <sup>3,4</sup>	%	22.81	15.70	68.83	0.00	50.00	24.62	18.54	75.30	5.00	65.00	55.00	46.0	83.64	0.00	100.00
Suspended matter	ml/wk	180.39	150.45	83.40	28.27	565.49	221.48	198.0	89.42	0.00	565.49	161.0	69.0	42.86	77.0	294.00
Buffer strip width <sup>3</sup>	m	11.56	7.85	67.88	0.00	20.00	2.60	0.97	37.31	2.00	5.00	not measured				
Altitude	m	67.53	41.00	60.71	22.00	143.00	32.69	19.80	60.57	-5.00	68.00	not measured				

<sup>1</sup> intercorrelation in France (Spearman's rho > 0.8) <sup>2</sup> intercorrelation in France (Spearman's rho = -0.836) <sup>3</sup> intercorrelation in France (Spearman's rho = -0.817)

<sup>4</sup> intercorrelation in Finland (Spearman's rho = -0.802) <sup>5</sup> measured twice in 2005 <sup>6</sup> measured between 1998 and 2000; taken from the field study of Liess & von der Ohe (2005)

Table 2: Characteristics and measurement results of pesticides in French+Finnish streams.

Compound	Monit. program	Type <sub>1,2</sub>	Class <sup>2</sup>	LC50 (µg/L) <sup>2</sup>	Log K <sub>ow</sub> <sup>2</sup>	Max. conc. (µg/L) <sup>3</sup>	Max. TU
acetochlor	France	H	chloroacetamide	9000	4.14	1.920	-3.67
alachlore	France	H	chloroacetamide	10000	3.09	0.806	-4.09
α-endosulfan	France	I	organochlorine	75	4.74	0.076	-2.99
carbofuran	France	I	carbamate	38.6	1.52	0.715	-1.73
chlorfenvinphos	France	I	organic phosphorous acid	0.3	3.85	0.115	-0.42
fenpropidine	France	F	piperidine	500	2.59	0.059	-3.93
linuron	France	H	urea	120	3.00	0.097	-3.09
oxadiazon	France	H	oxadiazole	2400	4.91	0.071	-4.53
pirimicarb	France	I	carbamate	17	1.70	0.072	-2.37
tebuconazole	France	F	triazole	4200	3.70	0.070	-4.78
α-cypermethrin	Finland	I	pyrethroid	0.15	6.94	n.d.	n.d.
α-endosulfan	Finland	I	organochlorine	75	4.70	n.d.	n.d.
azoxystrobin	Finland	F	strobilurine	259	2.50	n.d.	n.d.
cyprodinil	Finland	F	pyrimidine	10	3.90	n.d.	n.d.
deltamethrin	Finland	I	pyrethroid	3.5	6.20	n.d.	n.d.
λ-cyhalothrin	Finland	I	pyrethroid	0.38	7.00	n.d.	n.d.
malathion	Finland	I	organic thio-phosphorous acid	1	2.75	n.d.	n.d.
sulfotep	Finland	I	organic thio-phosphorous acid	2	3.99	n.d.	n.d.
τ-fluvalinate	Finland	I	pyrethroid	1	6.70	n.d.	n.d.
trifluralin	Finland	F	dinitroaniline	245	4.80	0.001 <sup>4</sup>	-4.34

<sup>1</sup> H = Herbicide, F = Fungicide and I = Insecticide <sup>2</sup> taken from Tomlin (2001)

<sup>3</sup> n.d. = not detected <sup>4</sup> Time-weighted average concentration

The extract was gently evaporated to 0.3 ml under nitrogen. Residue analysis was performed on an Agilent 6890N GC linked to a Pegasus III time-of-flight (TOF) mass spectrometer (Leco, Mönchengladbach, Germany). Time-weighted average (TWA) water concentrations for the LDPE samplers were calculated according to distribution coefficients from Booij et al. (2003). TWA water concentrations were converted to peak water concentrations by multiplying the TWA concentrations by a factor of 10 (Schäfer, R.B., Paschke, A. and Liess, M., *unpublished data*). Although the sampling methods differed, we think that the outcomes are comparable as the results of passive sampling and runoff-triggered water sampling correlated very high (Pearson's  $r=0.995$ ) in another study on the French streams (Schäfer et al., in preparation).