Supporting Information for:

Picogram per liter detections of pyrethroids and organophosphates in surface waters using passive sampling

Christoph Moschet[§,‖], *Etiënne L. M. Vermeirssen*[¦], *Remo Seiz*[§,×], *Hildegard Pfefferli*[±], *Juliane Hollender*[§,‖,*]

§ Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

‖ Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, 8092 Zürich, Switzerland

¦ Swiss Centre for Applied Ecotoxicology Eawag/EPFL, 8600 Dübendorf, Switzerland

× Zurich University of Applied Sciences, Institute of Life Sciences and Facility Management, 8820 Wädenswil, Switzerland

± Intercantonal Laboratory Schaffhausen, 8200 Schaffhausen, Switzerland

*** Corresponding author. Present address:**

Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland. Tel: +41 58 765 54 93. E-mail: juliane.hollender@eawag.ch

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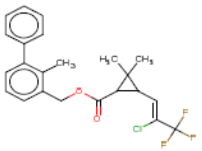
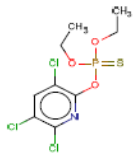
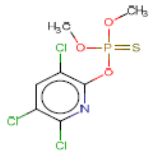
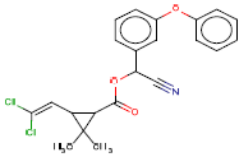
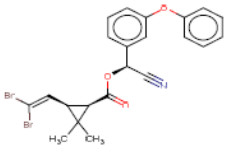
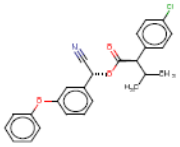
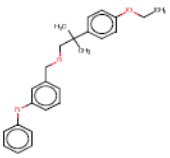
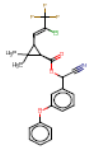
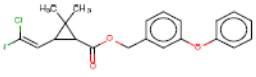
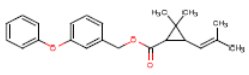
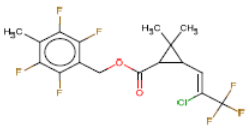
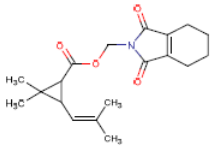
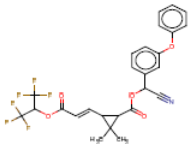
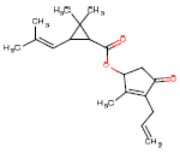
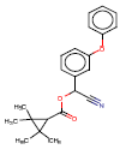
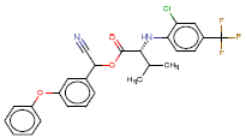
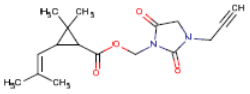
SI-1 Substance Information and Analytical Parameter

SI-1.1. Substance properties of all investigated analytes[a]

Substance Name	Cas-No.	Chemical Formula	Molecular Mass (g/mol)	Structure	Photolyisis half-life in water (d)	Hydrolysis half-life in water (d)
Target Analytes						
Bifenthrin	82657-04-3	C23H22ClF3O2	422.88		12	Stable
Chlorpyrifos	2921-88-2	C9H11Cl3NO3PS	350.89		29.6	25.5
Chlorpyrifos-methyl	5598-13-0	C7H7Cl3NO3PS	322.53		5.5	21
Cypermethrin (alpha)	52315-07-8	C22H19Cl2NO3	416.3		13	179
Deltamethrin	52918-63-5	C22H19Br2NO3	505.2		48	Stable
Esfenvalerat	66230-04-4	C25H22ClNO3	419.9		10	-
Etofenprox	80844-07-1	C25H28O3	376.49		6.3	Stable
lambda-Cyhalothrin	91465-08-6	C23H19ClF3NO3	449.85		40	Stable
Permethrin	52645-53-1	C21H20Cl2O3	391.3		1	31

Substance Name	Cas-No.	Chemical Formula	Molecular Mass (g/mol)	Structure	Photolyisis half-life in water (d)	Hydrolysis half-life in water (d)
Target Analytes						
Phenothrin	26002-80-2	C23H26O3	350.46		-	-
Tefluthrin	79538-32-2	C17H14ClF7O2	418.73		11.2	Stable
Tetramethrin	7696-12-0	C19H25NO4	331.41		-	-
Performance Reference Compounds						
Acrinathrin	101007-06-1	C26H21F6NO5	541.44		2.3	Stable
Allethrin	584-79-2	C19H26O3	302.41		-	-
Fenpropathrin	39515-41-8	C22H23NO3	349.42		14	1130
Fluvalinat (tau)	102851-06-9	C26H22ClF3N2O3	502.9		4	22.5
Imiprothrin	72963-72-5	C17H22N2O4	318.37		-	58.6

[a] all information taken from the Footprint database (University of Hertfordshire (2013)). Chemical structures were drawn from smiles codes with the program Jchem for Excel (ChemAxon). – no data for half-lives available.

SI-1.2. Detailed information of the used instruments

	GC-MS/MS (all environmal samples, final validation and elimination experiments)	**GC-MS (all experiments for optimization of the method)**
Gas chromatograph	Trace GC UltraTM Gas Chromatograph	Thermo Quest CE Instruments Trace GC Ultra Series Gas Chromatograph
Injector temperature	55°C	250°C
Injection volume	3 µL	3 µL
Injection mode	PTV with baffle liner	splitless (time 1 min)
Split flow	20 mL/min	50 mL/min
Carrier gas flow (He)	1.2 mL/min, constant flow	1 mL/min, constant flow
Oven Program		
run time	59.8 min	28 min
start	55°C for 1 min	100°C for 1 min
ramp	+30°C/min to 140°C (2.8 min); +2°C/min to 252°C (56 min)	+15°C/min to 280°C (12 min)
hold	-	280°C for 15 min
Column type	Zebron ZB-5MS (15m, 0.25 mm inner diameter, film thickness 0.25 µm)	RTX-5MS (15m, 0.25 mm inner diameter, film thickness 0.1 µm)
Mass spectrometer	Thermo Scientific TSQ Quantum GC, Triplequadropol	Thermo Scientific DSQ II Mass Spectrometer
Transfer line temperature	240°C	220°C
source temperature	230°C	250°C
ionization mode	positive electron ionization (EI)	positive electron ionization (EI)
Detection mode	selected reaction monitoring (SRM)	fullscan
Isolation window (m/z)	transitions see Table 1 in main text	50-350

SI-2 Experiments for the estimation of specific sampling rates

SI-2.1. Kinetic experiments for estimating the elimination of pyrethroids/organophosphates from silicone rubber (SR)

Kinetic parameters for the exchange of pyrethroids and organophosphates between silicone rubber (SR) and water were tested by two approaches. In the first approach, a kinetic experiment in a flow channel system as described in Vermeirssen et al. (2008) was set up for testing the elimination of all analytes (targets and performance reference compounds (PRCs)) from SR sheets (Fig SI-3.1). Two flow channels were run with a flow velocity of 0.23±0.02 m/s. Water from the nearby Chriesbach river was pumped into a storage tank. The water was run through the channels and pumped back at a rate of 20 m^3/h. Freshwater was added at 0.24 m^3/h in order to exchange the water in the system (0.48 m^3) within 2 h.

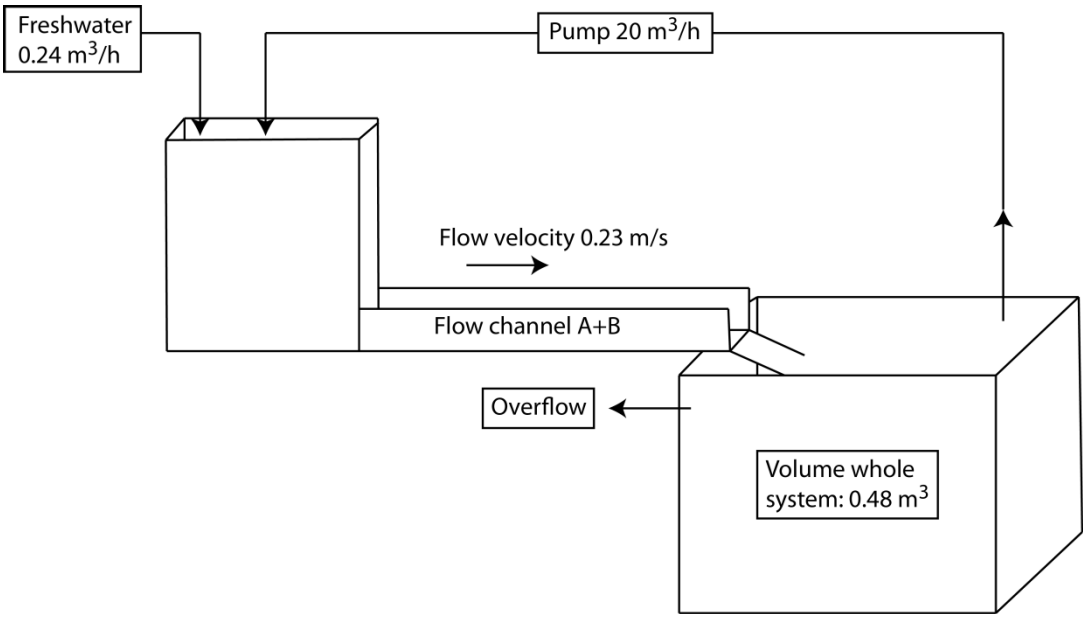


Fig. SI-2.1. Set-up of the flow channel system.

Thirty-four SR sheets with a size of 3 x 10 cm^2 were loaded with a mix of all substances analogue to the method described in Smedes and Booij (2012) to achieve a concentration of approximately 1 mg/L in the final extract. For this, 15 µg of each substance was spiked into a glass bottle filled with 70 mL methanol and the 34 sheets were added. The bottle was shaken for seven days with daily addition of nanopure water up to a water content of 60%. The loaded sheets were placed into the two flow channels for different time periods. During the whole experiment, temperature was measured, flow velocities were checked and the whole system was shaded with a black cover to prevent biofouling and photolysis. At the following 17 time points, one passive sample was taken from each channel: 0, 0.5, 1, 1.5, 2, 3, 4, 7, 10, 14, 23, 30, 35, 42, 49, 56, 60 days. In addition, non-spiked samples (blank) were taken at five time points (10, 14, 35, 49, 60 days). All samples were extracted and measured with the optimized method described in the main text.

In the second approach, 28 of the 40 environmental samples from the medium sized rivers (see Fig. SI-3.1) were spiked with five pyrethroids that were possible candidates for PRCs (allethrin, imiprothrin, acrinathrin, fluvalinate, fenpropathrin, Table SI-3.2). The five pyrethroids were the only substances that are not allowed to be used in Switzerland, neither in plant protection products nor as biocide. Two concentrations were selected: 1 mg/SR sheet (30 x 10 cm^2) and 0.5 mg/SR sheet (Table SI-3.2). The addition of the substances was done by spiking the exact volume of the PRC mix with 30 droplets onto the SR sheet. The sheets were dried under the hood (overnight) and were deployed for two weeks in the six medium-sized rivers. Six reference SR sheets were also spiked with the same concentration of PRC mix (Table SI-3.2). These sheets were not deployed in water, but stored in the dark at room temperature. After deployment, environmental sheets and the corresponding reference sheets were stored at -20°C and analyzed as described in the main text.

SI-2.2. Estimation of the elimination constant in the flow channel experiment

Because the exchange of non-polar substances between SR and water is isotropic (Rusina et al. (2010)), the determination of an elimination constant is a possible approach to calculate sampling rates. A clear elimination of the two substances with the lowest $logK_{ow}$ values (imiprothrin 2.9 and chlorpyrifos-methyl 4.3, respectively) from the SR over the whole 60 days was found in the flow channel experiment (see Fig. SI-2.2 A for the example of chlorpyrifos-methyl). Substances with $logK_{ow}$ values above 5 (except tefluthrin) were not eliminated at all during the 60 days of the experiment (see Fig. SI-2.2 C for the example of etofenprox). Questions arise for substances with medium $logK_{ow}$ values such as chlorpyrifos and allethrin (5.0 and 4.8, respectively). A clear elimination was visible over the first 7-14 days (see Fig. SI-2.2 B for chlorpyrifos). After this period, however, no further elimination occurred. For chlorpyrifos, natural occurrence of the substance in the river water could be the reason for this observation (peaks in blank samples after 14 days were present), for allethrin, there must be another reason. A non-homogenous distribution in the sheet can be excluded as the substances were loaded onto the sheet by using a water/methanol mixture and not by spiking the sheets with droplets. A reduction of the diffusion due to a biofilm or chalk deposition could be another reason.

For five substances (chlorpyrifos, chlorpyrifos-methyl, imiprothrin, allethrin, tefluthrin), an elimination constant (k_e) could be calculated for the first 14 days of deployment (see Fig. SI-2.3) by equation 1:

$$Retained\ fraction\ (f) = \frac{N(t)}{N(0)} = exp(-k_e \times t), \qquad (1)$$

where *N(t)* is the amount in the SR at time point *t* and *N(0)* is the initial amount of substance in the SR. A slight correlation between $logK_{ow}$ and $logk_e$ was found (Fig. SI-2.3), but much less pronounced than found for PAHs by Rusina et al. (2010).

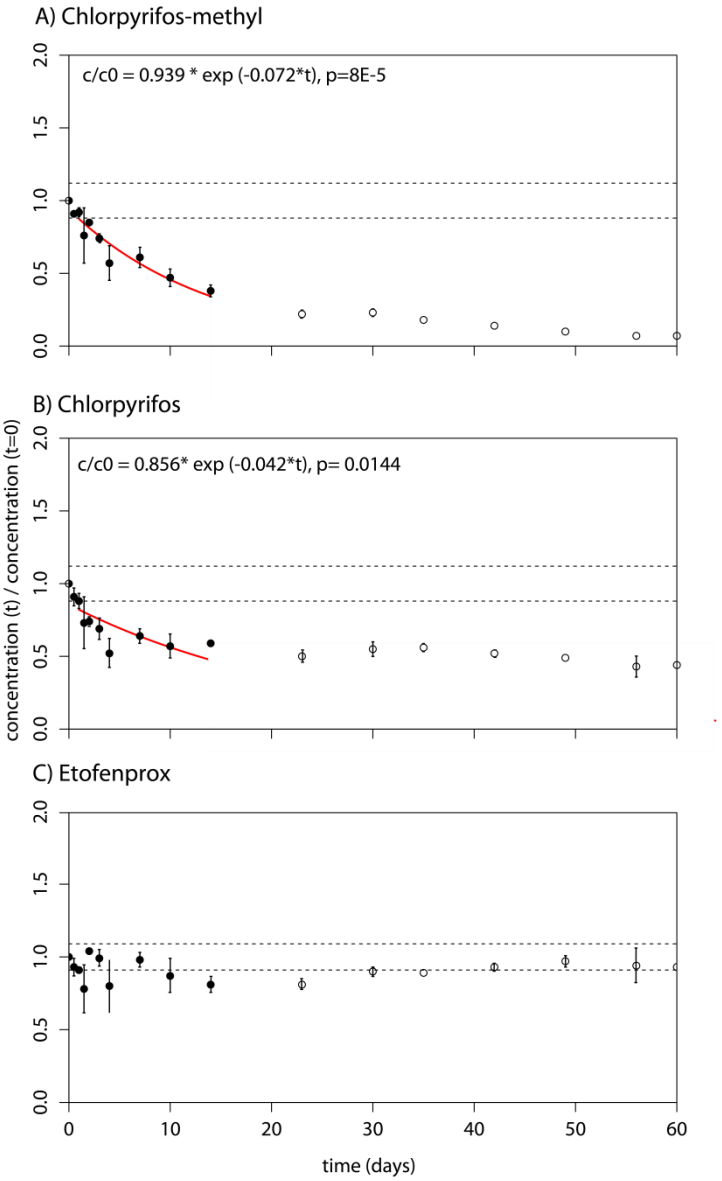


Figure SI-2.2. Elimination of three substances with different $logK_{ow}$ values from the SR in the flow channel experiment. A) chlorpyrifos-methyl ($logK_{ow}$ 4.3), B) chlorpyrifos ($logK_{ow}$ 5.0), C) etofenprox ($logK_{ow}$ 7.1). A regression could be fitted for the first 14 days (black dots) for chlorpyifos-methyl and chlorpyrifos (red line, p equals the statistical p-value of the regression). Uncertainty bars show the standard deviation from the two flow channels.

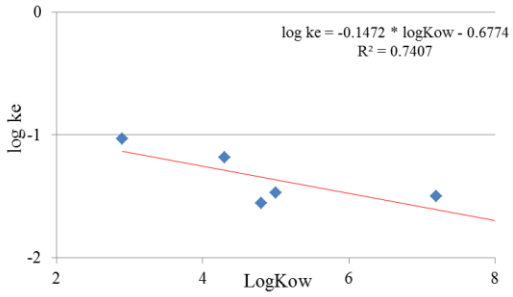


Figure SI-2.3. Correlation between $logK_{ow}$ and $logk_e$ values for the five substances (imiprothrin, chlorpyrifos-methyl, chlorpyrifos, allethrin, tefluthrin) that showed an elimination within 14 days of the experiment. Red line shows the linear regression.

SI-2.3. Estimation of distribution coefficients between SR and water (K_{pw})

When k_e values are measured properly, laboratory sampling rates (Rs) can be calculated from ke values with the following equation (Rusina et al. (2010)):

$$R_s = k_e \times m_{SR} \times K_{pw}, \qquad (2)$$

where m_{SR} is the mass of the sampler and K_{pw} is the distribution coefficient between SR and water. As R_s is directly proportional to the K_{pw} value, it is important to have accurately measured K_{pw} values (Rusina et al. (2010)). For an in-situ measurement of sampling rates, this is especially true for the substances used as PRCs. For the target substances which do not reach equilibrium within the sampling period, an estimation of K_{pw} from an empirical correlation is sufficient because the extrapolation of the sampling rate from PRCs to targets compounds only shows a weak correlation with K_{pw} (Smedes and Booij (2012), Rusina et al. (2010)). In comparison to PCBs and PAHs (Smedes et al. (2009)), for pyrethroids and organophosphates, no measured K_{pw} values exist for the material we used (Altesil^{TM}). K_{pw} values for some pyrethroids (Hunter et al. (2009), Lao et al. (2012), Bondarenko et al. (2007)) and organophosphates (Magdic et al. (1996)) for SR from different manufacturers are available in the literature, but the values for the pyrethroids only cover a narrow $logK_{ow}$ range between 6 and 6.5. Difilippo and Eganhouse (2010) found that differences in K_{pw} values derived for SR from different manufacturers and between SR with different thickness are

insignificant. Nevertheless, values for pyrethroids between the three studies differed up to a factor of six. Reasons for this could be different approaches used to determine K_{pw} values. In such experiments, it is important that there is negligible depletion of the substances in the water phase, that there is no sorption to equipment and that equilibrium is reached (Difilippo and Eganhouse (2010)). No correlation between $\log K_{ow}$ and $\log K_{pw}$ values were found for pyrethroids. Due to different functional groups that determine the polarity of the pyrethroids, an empirical correlation can *per se* not be expected for this substance class (compared to PCBs or PAHs).

Thus, it is essential that in further studies, K_{pw} values for pyrethroids and organophosphates are measured exactly and are determined for the used material. With this information available, sampling rates under defined conditions (e.g. flow channel) can be calculated for all substances. If an empirical correlation between $\log K_{ow}$ and $\log K_{pw}$ exists, the extrapolated K_{pw} values can be used to determine in-situ sampling rates by using PRCs. In addition, experiments that determine the duration of linear uptake of pyrethroids/organophosphates would help for the understanding of the kinetic behavior of the investigated substances. It is possible that smaller substances are already in equilibrium after a two week deployment in the river (personal communication Kees Booij, NIOZ, The Netherlands).

SI-2.4. Suitable performance reference compounds (PRCs)

Original PRC methods focused on PRCs for which between 20-80% are retained in the sheet after the deployment time (Booij and Smedes (2010)). Often, only one substance was used as PRC in a sample. A new method, the nonlinear least squares (NLS) method, developed by Booij and Smedes (2010), makes use of multiple PRCs with different environmental properties, e.g. at least six substances covering a $\log K_{ow}$ range of 3.5-5.5 with a distance of 0.3 log units (Smedes and Booij (2012)). The PRC must not be present in the environment,

that is, either isotope labeled substances or substances that are not allowed/used in the study area have to be selected. For substances such as PCBs and PAHs, there are enough substances from the same substance class available, either deuterated ones or substances that have not been produced in Europe. For pyrethroids and organophosphates, however, only a limited set of substances are possible candidates for PRCs. Only few isotope labeled substances are commercially available. Most of them were already used as internal standards in the analytics of this study (see main text). Five pyrethroids were selected that are not permitted in Switzerland: acrinathrin, allethrin, imiprothrin, fenpropathrin, and fluvalinate. From them, only allethrin fulfills the above mentioned $\log K_{ow}$ criterion. The $\log K_{ow}$ value of imiprothrin (2.9) is too low, while for the other substances it is too high (>5.5). It is therefore very important that more suitable PRCs for pyrethroids are made available, e.g. by synthesizing more isotope labeled pyrethroids. It may also be possible that other chemical classes (e.g. PCBs) are suitable as PRCs for the determination of in-situ sampling rates of pyrethroids and organophosphates. For this, it has to be confirmed if the diffusion of pyrethroids and organophosphates are also water boundary layer controlled, as it is the case for PCBs and PAHs (Kees Booij, NIOZ, The Netherlands, personal communication).

SI-2.5 Elimination of PRCs from environmental samples

In the second approach, the elimination of the five PRCs from SR sheets deployed in the environment was checked. An elimination of four of the five PRCs could be observed in most of the deployed SR sheets. For imiprothrin and allethrin, this was expected from their $\log K_{ow}$ values, but for acrinathrin and fenpropathrin, this was not expected. No correlation between flow velocities and retained fraction was observed (Fig. 2.4 for the examples of imiprothrin and acrinathrin). A correlation was expected as the increase in flow velocity strongly increases the sampling rate (Vermeirssen et al. (2009)). It is, however, not clear up to which flow velocity an increase in the sampling rate occurs. For this, kinetic experiments should be

carried out at different flow velocities. Other factors than the flow velocity were expected to be less significant. Biofouling was expected to be of less relevance because the investigated samples did not show significant biofouling. The temperature increased by maximal 15°C within the five month of investigation. This should have less effect than a factor of two (Booij et al. (2002)).

There are two hypothesis why no correlation was observed and why also very non-polar substances showed an elimination in the environmental samples. First, spiking of the sheets with PRCs (dripping droplets onto sheet and let it dry overnight) could lead to an inhomogeneous distribution of the substances in the sheet. This could lead to a faster and less homogenous elimination from the sheets. It is therefore important to determine the diffusion of pyrethroids and organophosphate in the SR sheets. Previous investigations showed that the spike method is less reliable than the loading method (personal communication Kees Booij, NIOZ, The Netherlands and Markus Zennegg, Empa, Switzerland).

Second, the PRCs could have undergone photolysis in the SR sheets. An elimination of PRC due to photolysis was already described for PAHs in semi-permeable membrane devices (SPMD) by Komarova et al. (2009). As the investigated PRCs have low photolysis half-lives in water (< 14 d, see Table SI-1.1, University of Hertfordshire (2013)), the photolysis in the SR could also be of relevance. Interestingly, a correlation between the elimination of imiprothrin and allethrin was found (Fig. SI-2.5 A); these are the two substances for which a *real* desorption can be expected. It is reasonable that substance behave similar when the elimination is due to the same process. It is, however, not sure that the flow velocity was the driving factor. On the other hand, no correlation between imiprothrin and acrinathrin elimination was found (Fig. SI-2.5. B). When the acrinathrin elimination was due to photolysis and imiprothrin elimination due to desorption, it is reasonable that there is no correlation between the two substances.

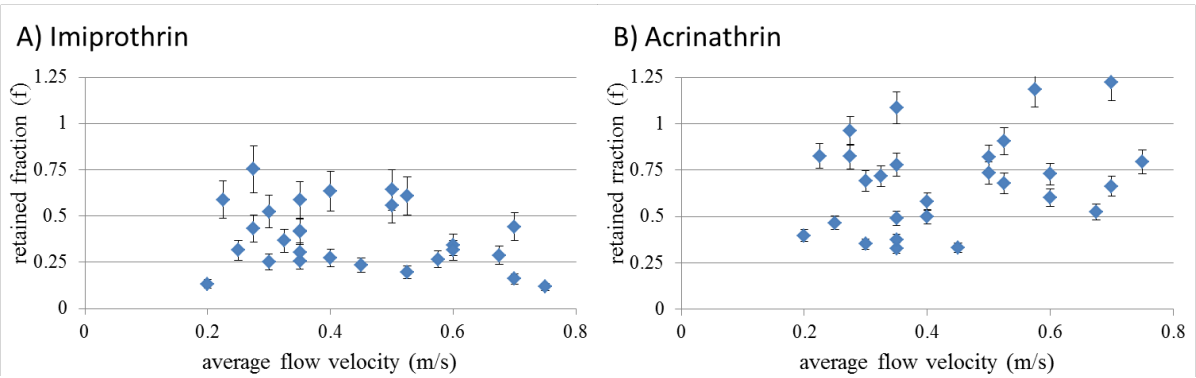


Fig SI-2.4. Retained fraction (f) of (A) imiprothrin and (B) acrinathrin at different flow velocities (average measurement at beginning and end of deployment) in the 28 spiked environmental samples. Error bars show the uncertainties of the analysis (see Table 1 in main text).

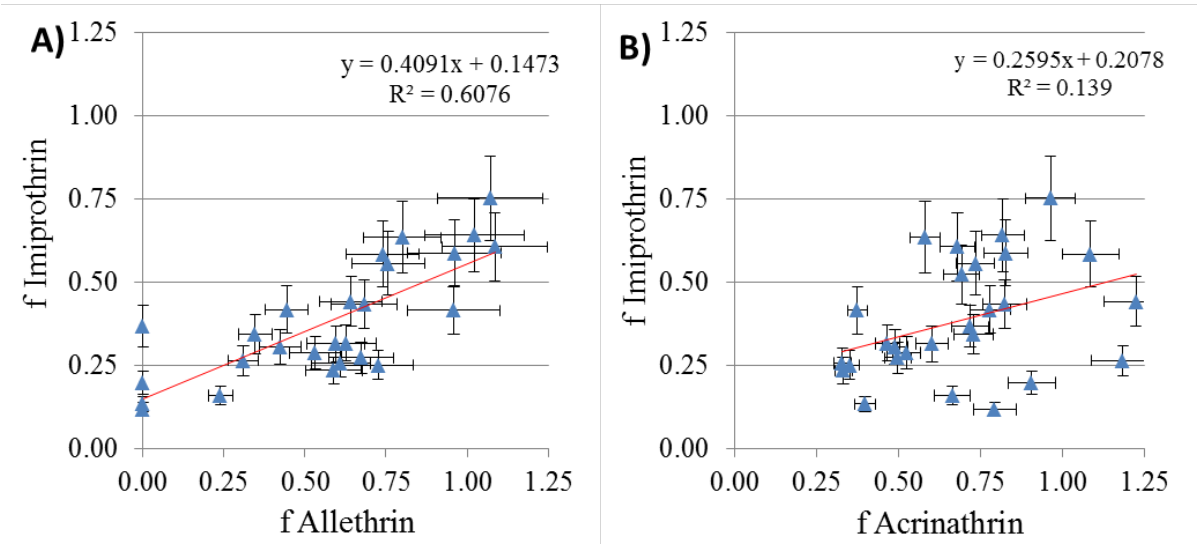


Fig SI-2.5. Comparison of the retained fraction (f) between (A) allethrin and imiprothrin and (B) acrinathrin and imiprithrin in the 28 spiked environmental samples. Error bars show the uncertainties of the analysis (see Table 1 in main text).

SI-3 Field Study Information

SI-3.1 Map of the study site

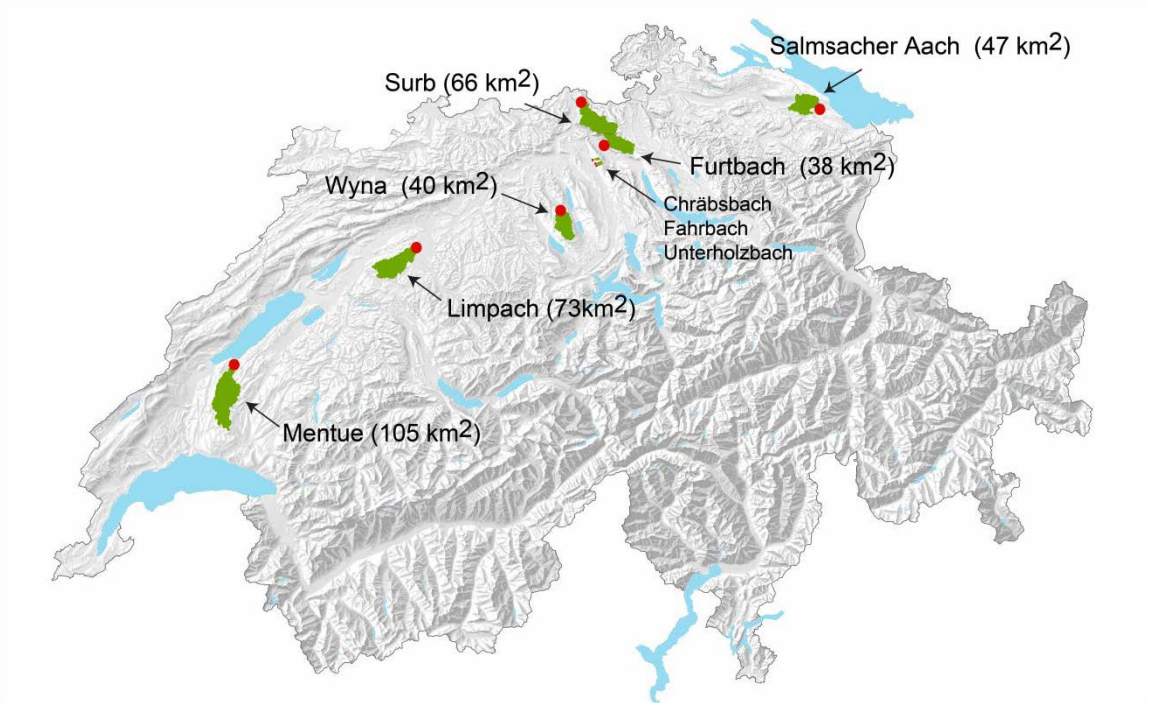


Figure SI-3.1. Map of Switzerland with the field study sites (catchments: green, sampling locations: red dots) of the 6 medium-sized rivers and the three small streams. Catchment sizes are indicated in brackets, if available.

SI-3.2 Sampling times and flow velocities

River Name / Sample Number	Date of deployment	Date of recovery	Deployment time (d)	Flow velocity at deployment (m/s)	Flow velocity at recovery (m/s)	Spike amount of PRC mix (mg/L)
Furtbach 1	09.03.2012	20.03.2012	11	0.65	0.65	
Furtbach 2	20.03.2012	03.04.2012	14	0.65	0.5	1.0
Furtbach 3	03.04.2012	17.04.2012	14	-	0.7	1.0
Furtbach 4	17.04.2012	30.04.2012	13	0.80	0.6	1.0
Furtbach 5	30.04.2012	15.05.2012	15	0.10	0.3	0.5
Furtbach 6	15.05.2012	29.05.2012	14	0.30	0.75	0.5
Furtbach 8	11.06.2012	26.06.2012	15	0.75	0.75	0.5
Furtbach 9	26.06.2012	10.07.2012	14	0.75	0.7	
Furtbach 10	10.07.2012	23.07.2012	13	0.40	0.25	
Surb 1	09.03.2012	20.03.2012	11	0.25	0.4	
Surb 2	20.03.2012	04.04.2012	15	0.35	-	1.0
Surb 3	04.04.2012	18.04.2012	14	-	0.6	1.0
Surb 5	02.05.2012	16.05.2012	14	0.40	0.5	0.5
Surb 6	16.05.2012	30.05.2012	14	0.50	0.15	0.5
Surb 8	13.06.2012	27.06.2012	14	0.40	0.4	0.5
Surb 9	27.06.2012	10.07.2012	13	0.30	0.35	
Surb 10	10.07.2012	23.07.2012	13	0.35	0.35	
Limpach 2	19.03.2012	03.04.2012	15	0.25	0.2	1.0
Limpach 3	03.04.2012	17.04.2012	14	0.15	0.4	1.0
Limpach 4	17.04.2012	30.04.2012	13	0.60	-	1.0
Limpach 5	30.04.2012	15.05.2012	15	0.35	0.15	0.5
Mentue 2	19.03.2012	03.04.2012	15	0.25	0.3	1.0
Mentue 3	03.04.2012	17.04.2012	14	0.35	0.7	1.0
Mentue 4	17.04.2012	30.04.2012	13	0.65	0.7	1.0
Mentue 5	30.04.2012	15.05.2012	15	0.65	0.05	0.5
Salmsacher Aach 2	20.03.2012	04.04.2012	15	0.50	-	1.0
Salmsacher Aach 3	04.04.2012	18.04.2012	14	-	0.4	1.0
Salmsacher Aach 4	18.04.2012	02.05.2012	14	0.40	0.3	1.0
Salmsacher Aach 6	16.05.2012	30.05.2012	14	0.30	0.3	0.5
Salmsacher Aach 7	30.05.2012	14.06.2012	15	0.20	0.4	0.5
Salmsacher Aach 8	14.06.2012	27.06.2012	13	0.40	0.3	0.5
Wyna 2	19.03.2012	03.04.2012	15	0.60	0.1	1.0
Wyna 3	03.04.2012	17.04.2012	14	0.20	0.8	1.0
Wyna 4	17.04.2012	30.04.2012	13	-	0.3	1.0
Chräbsbach 1	03.04.2013	15.04.2013	14	0.05	-	
Chräbsbach 2	15.04.2013	30.04.2013	14	0.05	-	
Fahrbach 3	30.04.2013	14.05.2013	14	-	0.4	
Fahrbach 4	14.05.2013	28.05.2013	14	-	0.3	
Unterholzbach 1	03.04.2013	15.04.2013	14	0.05	-	
Unterholzbach 2	15.04.2013	30.04.2013	14	0.4	-	
Reference Blank 2						1.0
Reference Blank 3						1.0
Reference Blank 4						1.0
Reference Blank 5						0.5
Reference Blank 6						0.5
Reference Blank 8						0.5

- Flow velocity could not be determined

SI-3.3 Estimated concentrations from the measurements in the field (ng/L)[1]

River Name / Sample Number	Bifenthrin	Chlorpyrifos	Chlorpyrifos-methyl	Cyper-methrin	Delta-methrin	Esfenvalerat	Etofenprox	Lambda-Cyhalothrin	Permethrin	Phenothrin	Tefluthrin	Tetra-methrin
LOD (environment)	0.006	-	0.06	0.008	-	-	-	0.10	-	0.10	-	-
LOQ (environment)	0.02	0.02	0.20	0.02	0.10	0.10	0.03	0.30	0.06	0.40	0.20	0.08
Furtbach 1		0.9	0.3	0.03	0.5							
Furtbach 2		0.7	<LOQ	<LOQ	0.3							
Furtbach 3		0.9	1	0.1	1			<LOQ				
Furtbach 4		0.8	0.3	0.1	2			<LOQ				
Furtbach 5		0.6	8	0.08	0.3			<LOQ				
Furtbach 6		0.9	1	0.07	0.7			0.5				
Furtbach 8		1	6	0.1	0.5			0.4	0.4			
Furtbach 9		2	1	0.06	0.3			<LOQ	0.8			
Furtbach 10		0.9	3	0.1	0.8			0.4	0.4			
Surb 1		0.3										
Surb 2		0.4		0.03								
Surb 3		0.5		0.03					0.07			
Surb 5		0.3		0.06					0.1			
Surb 6		0.3		0.09								
Surb 8		10		0.03					0.08			
Surb 9		2		0.04					0.2			
Surb 10		0.5		0.05					0.2			
Limpach 2		0.3		0.04								
Limpach 3	<LOQ	0.4		0.05								
Limpach 4	<LOQ	0.3		0.04								
Limpach 5		0.2		0.03								
Mentue 2		0.06		0.1	0.1							
Mentue 3		0.1		0.04								
Mentue 4		0.1		0.2								
Mentue 5		0.08		0.06								
Salmsacher Aach 2		0.1	0.6									
Salmsacher Aach 3		0.4	3									
Salmsacher Aach 4		0.3	2									
Salmsacher Aach 6		0.6	1									
Salmsacher Aach 7		0.5	0.2									
Salmsacher Aach 8		0.4	3									
Wyna 2												
Wyna 3		0.1					0.2					
Wyna 4		0.04										
Chräbsbach 1												
Chräbsbach 2		0.08	<LOQ									
Fahrbach 3		1										
Fahrbach 4		0.5										
Unterholzbach 1												
Unterholzbach 2		0.5	2									

[1] uncertainties of the quantification: factor 3 in both directions (see main text). LOD: limit of detection, LOQ: limit of quantification. - if a signal was present in the blank samples, only LOQ was determined by 10 times the intensity of the blank value.

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