Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.
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Supplementary information

SI 1 Pulse function

The concentration peaks are fitted to an empirical function of the following type:

$$y = y_0 + A\left(1 - e^{-\frac{x - x_0}{t_1}}\right)^p e^{-\frac{x - x_0}{t_2}}$$

With y_0 = offset, x_0 = center, A= amplitude, t_1 = width, p = power, t_2 = width.

There is no physical meaning behind the parameters. They only serve to mimic peak chemographs within floodwaves with their typical tailed phasing out.

Fittings were done with Origin 75E or with Microsoft Excel using the solver algorithm.

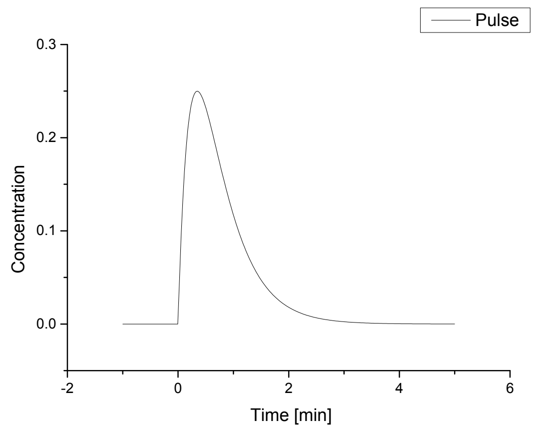

Figure 1: Pulse function mimicking a flood wave concentration peak

SI 2 Precipitation records

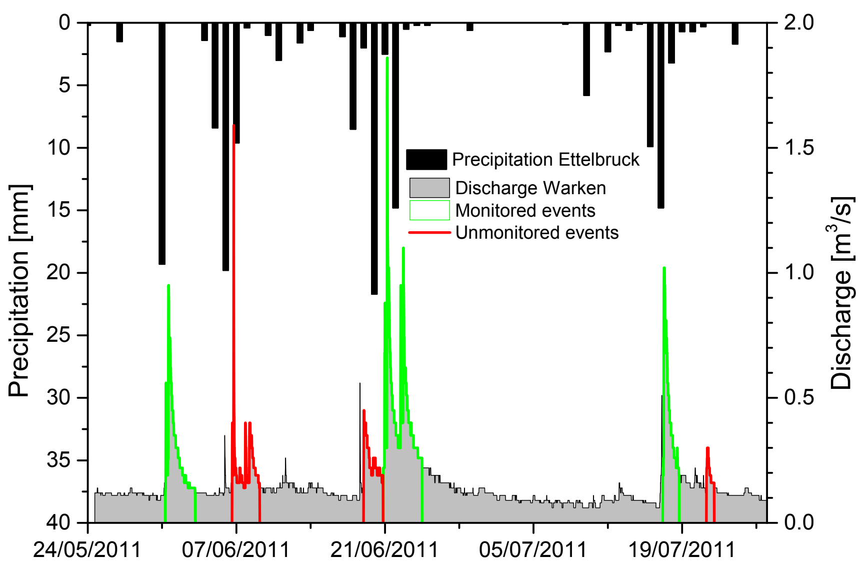

Figure 2: Monitoring period through spring 2011 showing precipitation from the gauge in Ettelbruck near the outlet of the Wark basin.

SI 3 Passive sampler exposure periods : base-flow and flood event duration at the Warken gauge

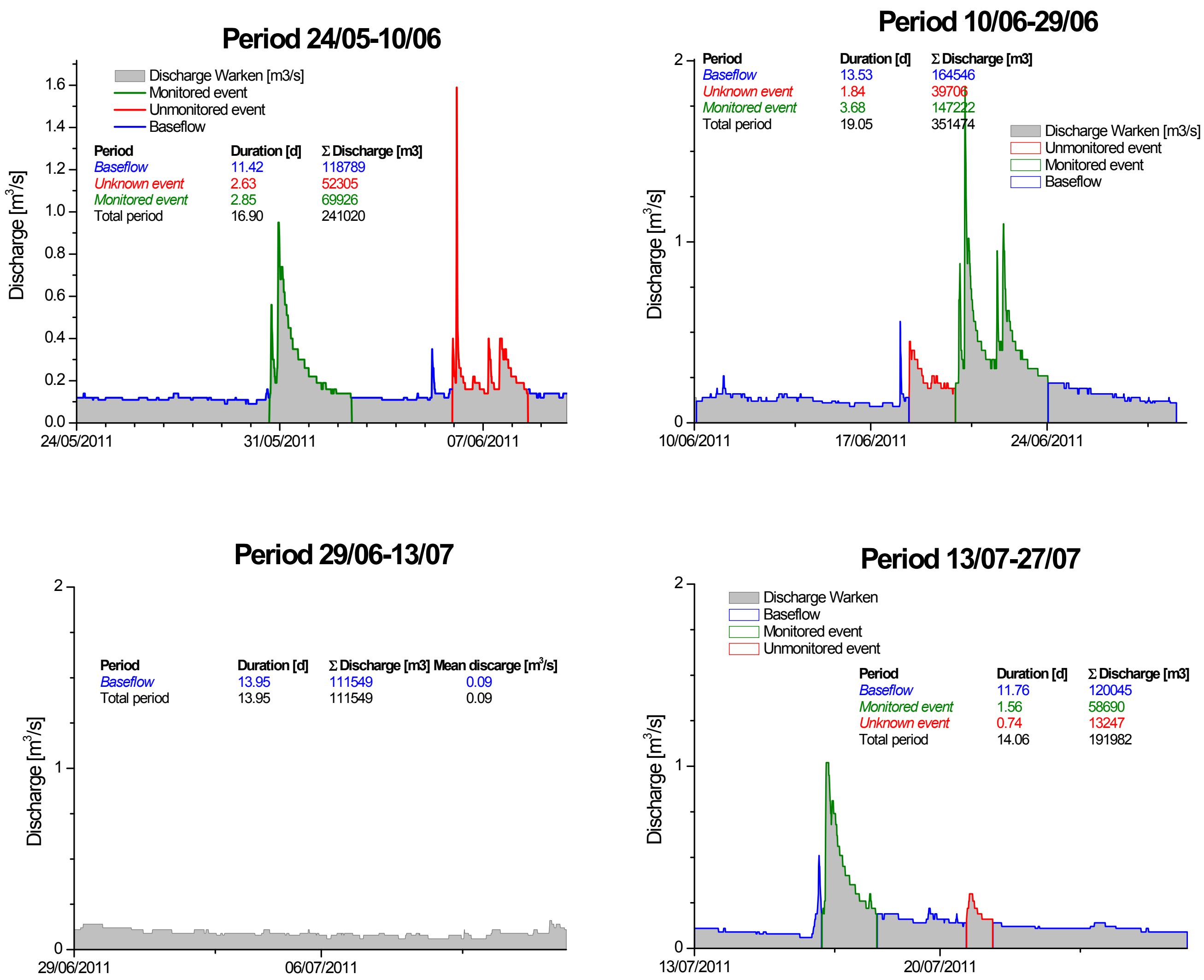

Figure 3: Hydrological conditions during the four passive sampler exposure periods of relevance for this study.

SI 4 Compound specific sampling rates used in this study

Table 1: Sampling rates used in the calculations of the study. The sampling rates were calculated from grab samples and passive-sampler masses in the low-flow period from June 29th to July 13th where possible (detections in passive samplers and grab samples)

Sampling rates [L/d]	Terbuthyla-zine	Flufena-cet	Metola-chlor	Iso-proturon	Carba-mazepine	Metolachlor-ESA
1 Mertzig	**0.284**	**0.179**[1]				
2 Turel	**0.176**	**0.179**				
3 Mechelbach	**0.176**[2]	**0.179**				
4 Fel	**0.176**	**0.179**				
5 Niederfeulen	**0.235**	**0.179**				
6 Warken	**0.380**	**0.232**	**0.171**	**0.191**	**0.227**	**0.082**

[1] Mertzig Rs was used for all other stations upstream to Warken. No detections for Turel, Mechelbach and Fel and an inconsistent Rs for Niederfeulen because of too low passive sampler masses/grab sample concentrations.

[2] Rs could not be determined for Mechelbach and Fel because either passive sampler mass or grab sample concentrations were below LOQ. Rs from Turel was used instead because of similar size of the streams.

SI 5 Pesticide dosage and environmental properties

Table 2: Terbuthylazine products authorized in Luxembourg in 2011 and their nominal dose.

Product	Active compounds	Dose [g ha^{-1}]
Successor T	Terbutylazine	750
	Pethoxamide	1200
Laddok T	Terbutylazine	700
	Bentazone	700
Gardo Gold	Terbutylazine	750
	Metolachlor	1250
Calaris	Terbutylazine	495
	Mesotrione	105
Aspect T	Terbutylazine	749
	Flufenacet	450

Table 3: SER-Statisitics of average active compound use in maize. The data is based on pesticide purchases by around 500 farms. Average doses show the popularity of an active compound. With 341 g ha^{-1} for terbuthylazine as average, it is used on 45 % of the maize surfaces (750 g ha^{-1} assumed as nominal dose)

Active compound	Average dose [g ha^{-1}]		
	2007	**2008**	**2009**
Terbuthylazine	341	330	341
Glyphosate	338	245	247
Bentazone	179	173	154
S-Metolachlor	144	126	150
Sulcotrione	132	119	106
Flufenacet	72	72	65
Dimethenamide-P	19	61	35
Pendimethaline	16	29	34
Mesotrione	23	18	24

Table 4: Investigated compound properties. Data from PPDB database[3]. $t_{1/2}$ is the "typical" value.

Compound	Log K_{ow} [-]	Log K_{OC} [L/kg OC]	$t_{1/2}$ [d]
Terbuthylazine	3.4	2.36	72
Flufenacet	3.5	2.6	20
S-Metolachlor	3.05	2.3	52
Bentazone	-0.46	1.74	20
Isoproturon	2.5	2.09	12
Metolachlor-ESA	-1.89	0.95	400
Desethyl-Terbutylazine	2.3	1.89	54
Sulcotrione	-1.7	1.56	25

[3] https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

SI 6 Land use data for the subcatchments in the Wark

Table 5: Catchment surfaces and land use data for the Wark monitored subcatchments.

				Land use[4]					Cultures 2011[5]			
Monitoring station	**Basin name**	**Basin area**	**Average slope**	**Impermeable surfaces**	**Grassland**	**Forest**	**Arable**	**WWTP capacity[6]**	**Cereals**	**Maize**	**Potatoes**	**Oilseed**
		[ha]	[°]	[ha]	[ha]	[ha]	[ha]	[PE]	[ha]	[ha]	[ha]	[ha]
1	Mertzig	1625	5.09	108	432	664	421	720	138	141	10	28
2	Turel	1269	8.25	108	35	695	538	275	178	63	1	43
3	Mechelbach	911	8.78	6	195	512	392	3050	97	26	6	30
4	Fel	882	9.30	0	0	460	422	0	142	20	8	29
5	Niederfeulen	4778	6.65	170	1010	1969	1630	5645	530	321	17	117
6	Warken	7651	8.67	216	1036	3562	2838	7415	851	430	36	196

[4] OBS data base of the Luxembourgish Cadastral Service
[5] FLIK data on field plot level, made available by the SER, Service d’Economie Rurale of the Luxembourgish Ministry of Agriculture.
[6] Capacity data of the Wastewater Treatment Plants (WWTP) summed up for each catchment

SI 7 Chemographs for other maize herbicides in the autosampled flood events

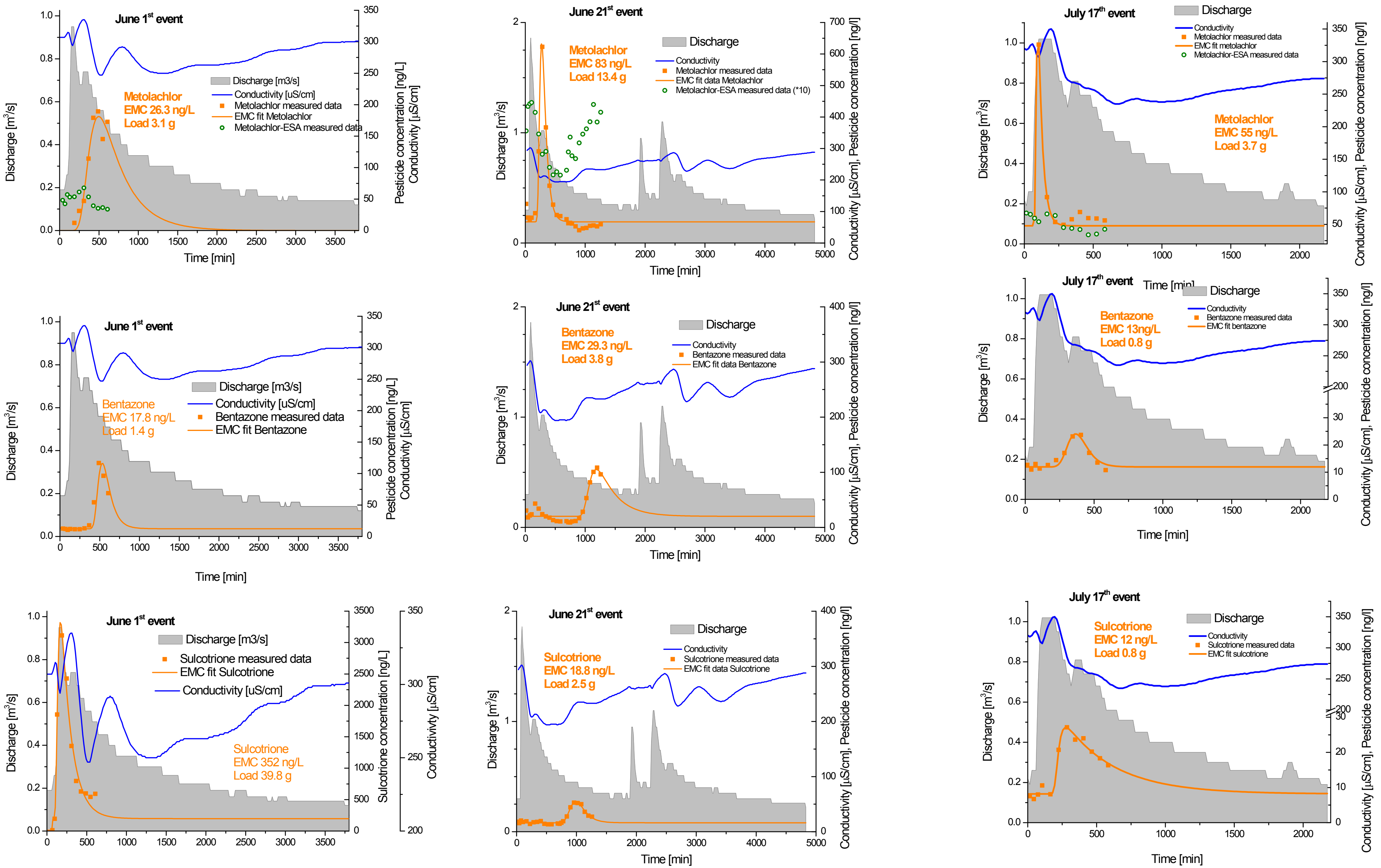

Figure 4: Chemographs for the three sampled evenst for metolachlor, bentazone and sulcotrione. The monitoring station is the outlet of the catchment (station 6).

SI 8 Passive sampler mass balance Flufenacet

Table 6: Flufenacet distribution between events and base-flow yielding the total collected mass for the Warken monitoring point. Grey coloured fields represent measured values. All other fields except duration were calculated by mass difference/EMC transformation. The sampling rate for flufenacet was 0.232 L/d

Period	POCIS mass exposure period [ng]	Period duration [d]	Baseflow			Event 1			Event 2		
			Duration [d]	TWA [ng/L]	Equivalent mass [ng]	Duration [d]	EMC [ng/L]	Equivalent mass [ng]	Duration [d]	EMC [ng/L]	Equivalent mass [ng]
24/05-10/06	186	16.9	11.42	3	8	2.85	46	30	2.63	148	242
10/06-29/06	81	19.05	13.53	2	6	1.84	45	105	3.68	35	30
29/06-13/07	6	13.95	13.95	2	6						
13/07-29/07	5	14.06	11.76	1	3	1.56	3	1	0.74	1	7

SI 9 WWTP outlet concentrations and global catchment balances

Five treatment plants in rural environments (both inside and outside the investigated catchment) were monitored with passive samplers at the outlet with the same exposure periods than in the river network. The results were used to calculate the contribution by WWTPs to the pesticide mass flow. WWTP outlets mirrored the use of active compounds in the catchments quite well. The pathway is probably cleaning of spraying devices in farm courtyards, which are connected to the public sewer

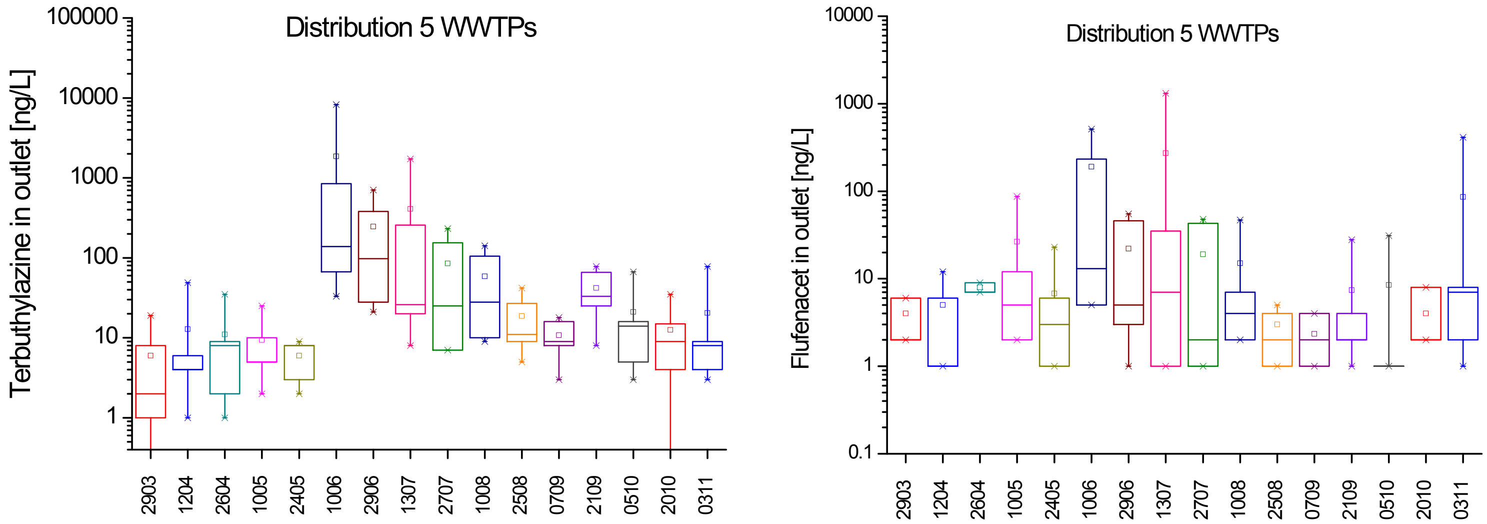

Figure 5: Tebuthylazine and flufenacet 14 day TWA concentrations in the WWTP outlets (n=5) starting mid-March until early-November 2011. Dates featured are the collection dates after a 14 day exposure.

system.

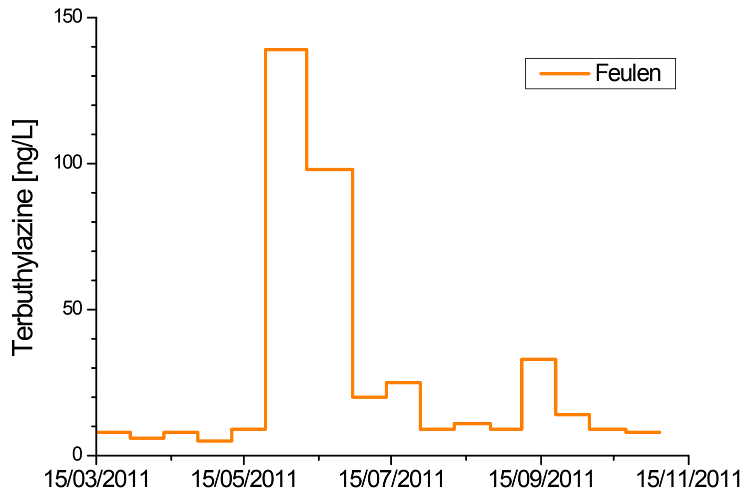

Figure 6: Terbuthylazine Time Weighted Average (TWA) for terbuthylazine in the WWTP outlet of Feulen.

The following loads were calculated from the EMCs of the flood waves and the TWA of the base-flow multiplied by the respective discharges of the (sub-)periods. Baseflow was split between groundwater and WWTP contribution based on the loads calculated for the treatment plants. The groundwater load was calculated by subtraction of WTTP loads from baseflow loads.

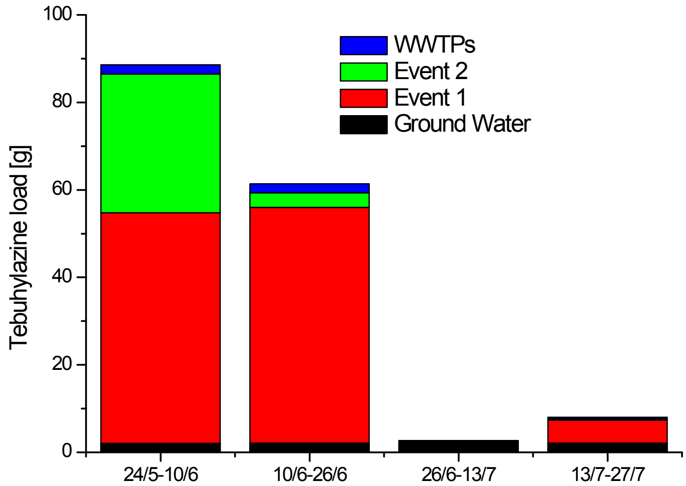

Figure 7: Absolute load distribution amongst the flow paths for each observation period.

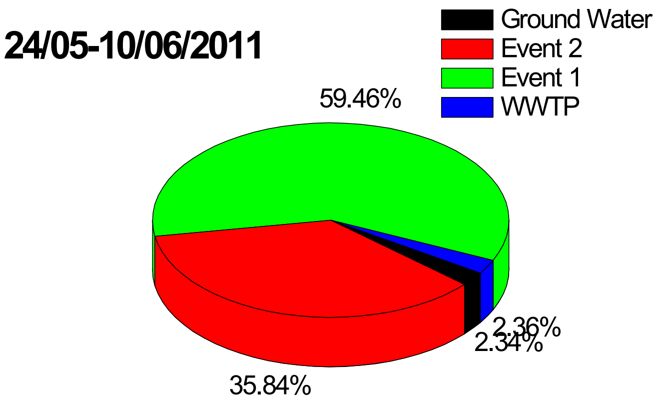

Figure 8: Flowpath fractions in percent

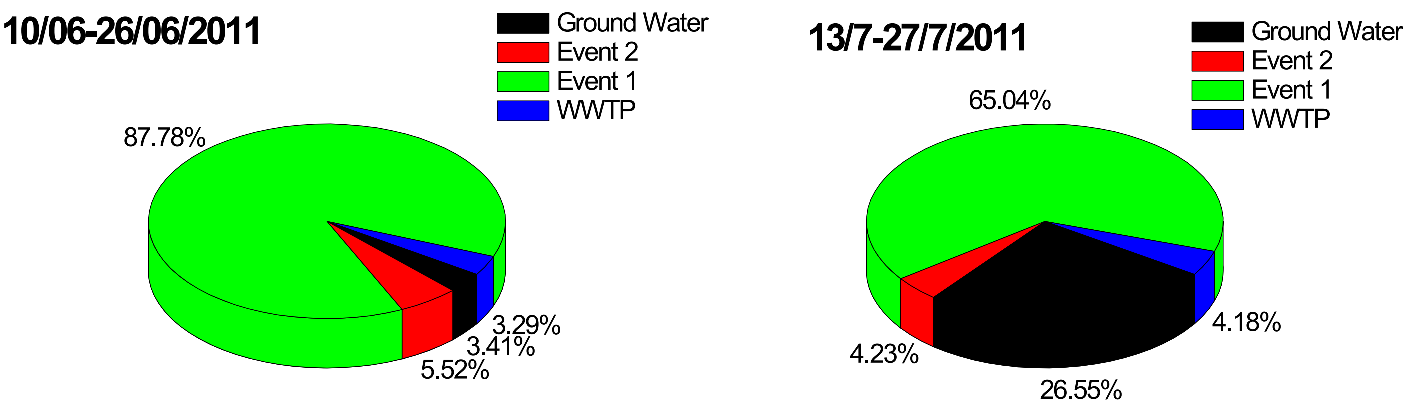

Figure 9: Flow path fraction continued for two following periods.

SI 10 Verifying the infinite sink character of POCIS passive samplers

We conducted a field trial to investigate the infinite sink character of the POCIS, i.e. that collected pesticide masses during a peak even will be kept in the sorbent even though ambient water concentrations fall to very low concentration in the aftermath of a peak. To this purpose, we spiked the POCIS in the lab with a cocktail of compounds and exposed them in the Wark river during November 2011. Spiked passive samplers were retrieved from the river after approx. 2, 6, 10 and 15 days and the remaining compound mass was determined. In parallel unspiked POCIS were exposed to monitor if any of the compounds were present during exposure time. Most of the compounds remained in the POCIS over 15 days, while some showed a significant decrease (Figure 7 & 8). First order decay constants could be fitted and half-lives calculated. With 14-days exposure period, a loss of less than 10% (analytical uncertainty) would require a half-life of 90 days for 13 days lag-phase after a peak, while 6 days of lag phase would need a half-life of 40 days. As can be seen from figure 9 compounds with a log K_{OW} > 1 are fulfilling that requirement. The behaviour is individual below log K_{ow} of 1 and needs to be evaluated on a case-by-case basis.

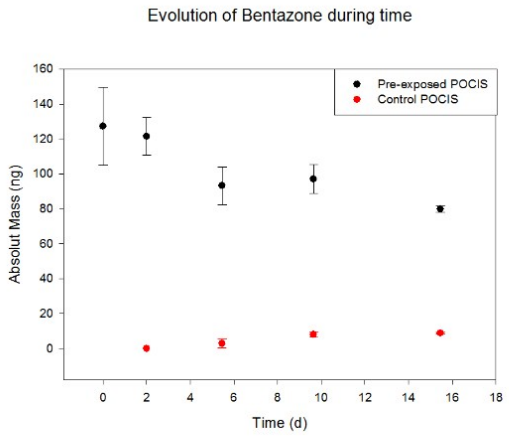

Figure 10: Recoveries of the bentazone spike during the 15

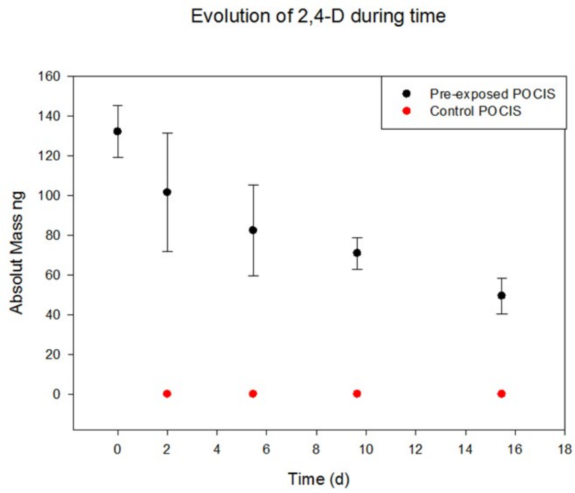

Figure 11. 2,4-D recovery in the POCIS over 15 days

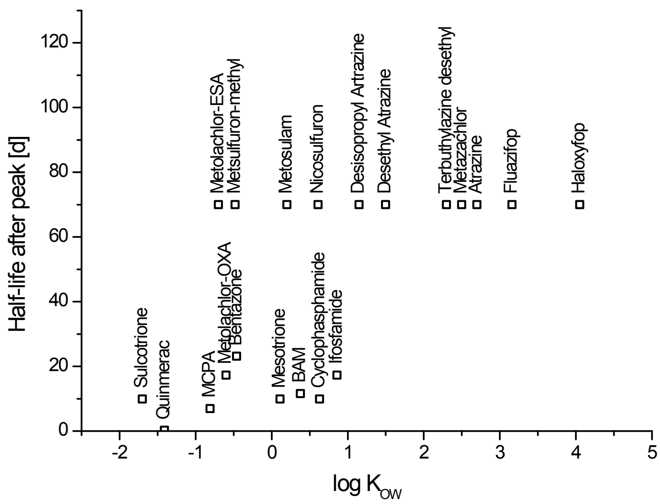

Figure 12: Summary of the half-lives of the compounds in relation to their log K_{OW}. Not all compounds are shown for readability.