Supporting Information

Pesticide Mass Budget in a Stormwater Wetland

*Elodie Maillard and Gwenaël Imfeld**

Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS), University of Strasbourg/ENGEES, CNRS, 1 rue Blessig, F-67 084 Strasbourg Cedex

**Corresponding author phone: + 333 6885 0407; Fax: + 333 8824 8284, e-mail: imfeld@unistra.fr*

Table S1. Physico-chemical characteristics of the bed sediments in the wetland forebay (Rouffach, Alsace, France). Analytical uncertainty is 5% for the major elements.

			Day 0 (March 23rd)			Day 84 (June 15th)			Day 168 (September 7th)		
			50 µm – 250 µm	250 µm - 1mm	>1mm	50µm – 250 µm	250 µm - 1mm	>1mm	50 µm - 250 µm	250 µm - 1mm	>1mm
Physico-chemical composition	OC	[%]	16.67	14.95	13.88	13.47	15.18	15.32	15.90	15.01	15.51
	SiO_2	[%]	49.47	49.62	48.62	49.90	49.60	49.10	50.20	50.30	49.50
	Al_2O_3	[%]	10.29	11.64	11.82	12.48	11.95	12.65	11.17	12.43	11.66
	MgO	[%]	2.04	2.24	2.23	2.15	2.03	1.97	1.93	2.09	1.98
	CaO	[%]	12.90	11.80	14.20	11.55	11.63	11.76	12.28	10.59	12.66
	Fe_2O_3	[%]	4.53	5.15	5.27	5.08	4.76	5.07	4.43	4.78	4.69
	MnO	[%]	0.08	0.09	0.08	0.09	0.08	0.08	0.07	0.07	0.08
	TiO_2	[%]	0.57	0.61	0.60	0.58	0.52	0.56	0.55	0.57	0.54
	Na_2O	[%]	0.61	0.45	0.45	0.40	0.40	-	0.60	0.40	0.40
	K_2O	[%]	2.10	2.36	2.39	2.55	2.55	2.72	2.32	2.70	2.50
	P_2O_5	[%]	0.39	0.36	0.32	0.22	0.21	0.21	0.25	0.21	0.21
	pH	[-]		7.64			n.a.			n.a.	
Texture	Clay	[%]		16			22			38	
	Silt	[%]		25			26			44	
	Sand	[%]		59			52			18	

Table S2. Physico-chemical properties of pesticides, and analytical limits and uncertainties for quantification in water, bed sediments and total suspended solids, and vegetation and invertebrates. Cyazofamid (CYA), cyprodinil (CYP), difenoconazole (DIF), dithiocarbamates (DIT), fludioxonil (FLU), glyphosate (GLY), AMPA, kresoxim methyl (KM), metalaxyl (MET), pyrimethanil (PYR), spiroxamine (SPI) and tetraconazole (TET).

	Unit	CYA	CYP	DIF	DIT	FLU	GLY	*AMPA*	KM	MET	PYR	SPI	TET
Water solubility (20°C[a] / 25°C[b])	[mg L^{-1}]	0.114[a] / 16.34 - 17.01[b]	13[a] / 12.38 - 13[b]	15[a] / 0.60 - 15[b]	2 - 6.2[a] / n.a.[b]	1.8[a] / 1.8 - 3.9[b]	10^{4}[a]/ 1.2 10^{4} - 10^{6}[b]	5.8[a] /10^{6}[b]	2.0[a] / 2.0 - 12.8[b]	2.6 10^{4}[a]/ 560 - 2.6 10^{4}[b]	121[a] / 121 - 165.8[b]	405[a] / 470[b]	156.6[a] / 3.8 - 156[b]
Log K_{ow}	[-]	3.2[a] / 2.87[b]	4[a] / 4.0[b]	4.36[a] / 4.30[b]	1.33[a] / n.a.[b]	4.12[a] / 4.12[b]	-3.2[a] / -4.0[b]	-1.63[a] / -2.17[b]	3.40[a] / 3.40[b]	1.65[a] / 1.65[b]	2.84[a] / 2.84[b]	2.89[a] / 5.51[b]	3.56[a] / 3.56[b]
K_d	[L kg^{-1}]	n.a.[a]	n.a.[a]	n.a.[a]	n.a. - 9.7[a]	n.a.[a]	5.3 - 810[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
K_{oc}	[L kg^{-1}]	n.a.[a] / 214 - 978[b]	n.a[a] / 1995 - 3571[b]	n.a.[a] / 11279 - 24230[b]	998 - 5 10^{5}[a] / n.a.[b]	1.4 10^{5}[a] / 1551 - 2362[b]	884 - 6 10^{4}[a] / 18[b]	n.a.[a] / 1.9[b]	n.a.[a] / 4.07 - 5482[b]	n.a.[a] / 22.6 - 352[b]	n.a.[a] / 536 - 835[b]	n.a.[a] / 437 - 948[b]	n.a.[a] / 1291 - 1.2 10^{5}[b]
DT50 aerobic-anaerobic soil	[day]	10 - n.a.[a]	126 - 183[a]	130 - n.a.[a]	0.1[a]	164 - n.a.[a]	96 - 22[a]	n.a.[a]	2 - 1[a]	n.a.[a]	n.a.[a]	25[a]	n.a.[a]
Aqueous photolysis DT50 (pH=7)	[day]	0.1[a]	13.5[a]	stable[a]	stable[a]	10[a]	69[a]	n.a.[a]	28[a]	stable[a]	stable[a]	50.5[a]	217[a]
Aqueous hydrolysis DT50 (20°C, pH=7)	[day]	25[a]	stable[a]	stable[a]	1.3[a]	stable[a]	stable[a]	n.a.[a]	34[a]	106[a]	stable[a]	stable[a]	stable[a]
EC50	[ppm]	0.19[a]	0.033[a]	0.77[a]	0.073[a]	0.4[a]	40[a]	n.a.[a]	0.186[a]	28[a]	2.9[a]	6.1[a]	3[a]
Water													
Detection limit	[µg L^{-1}]	0.03	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.01	0.02	0.02	0.02
Quantification limit	[µg L^{-1}]	0.1	0.02	0.05	0.05	0.05	0.1	0.1	0.1	0.02	0.05	0.05	0.05
Uncertainty	[%]	24	27	25	21	23	26	24	23	25	26	23	25
Extraction recovery	[%]	80-95	80-95	80-95	80-95	80-95	85-100	85-100	80-95	80-95	80-95	80-95	80-95
Bed sediments and TSS samples													
Detection limit	[µg $kg^{-1}_{d.w}$]	3	3	3	3	3	3	3	3	3	3	3	3
Quantification limit	[µg $kg^{-1}_{d.w.}$]	10	10	10	10	10	10	10	10	10	10	10	10
Uncertainty	[%]	33	32	26	45	32	36	37	28	27	30	35	28
Extraction recovery	[%]	50-60	50-60	50-60	50-60	50-60	40-50	40-50	50-60	50-60	50-60	50-60	50-60
Vegetation and invertebrates													
Detection limit	[µg kg^{-1}_{wet}]	3	3	3	3	3	3	3	3	3	3	3	3
Quantification limit	[µg kg^{-1}_{wet}]	10	10	10	10	10	10	10	10	10	10	10	10
Uncertainty	[%]	30	21	25	43	23	33	31	25	25	26	25	27
Extraction recovery	[%]	40-50	40-50	40-50	40-50	40-50	30-40	30-40	40-50	40-50	40-50	40-50	40-50

Sources: [a]Pesticide Properties Data Base (PPDB) (http://sitem.herts.ac.uk/aeru/projects/ppdb/index.htm)

[b]www.chemspider.com

Table S3. Analytical methods used to quantify pesticides in the different compartments of the studied stormwater wetland (Rouffach, Alsace, France).

Molecule	Method	Apparatus	Column	Quantification ion	Qualification ion	Mode
Cyazofamid	LC-MS-MS	API 4000 AB SCIEX	zorbax eclipse XDB-C18 2.1 x 50 mm	325	108	positive
Cyprodinil				226	93	positive
Difenconazole				406	251	positive
Fludioxonil				246.947	125.9	negative
Kresoxim methyl				314	116	positive
Metalaxyl				280	220	positive
Pyrimethanil				200	107	positive
Spiroxamine				298	144	positive
Tetraconazole				372	159	positive
[a]Glyphosate		API 3000 AB SCIEX		390.1	168.1	negative
[a]AMPA				332.17	110	negative
Dithiocarbamates (metiram-zinc + mancozeb)	GC-MS-MS (Headspace)	Agilent 6890 GC / 5973 MS	DB-624 30m x 0.25mm, 1.40µm	76	44	-

[a]The derivatization of glyphosate and AMPA prior to analyses was performed by adding 100 µL of a solution of borate buffer (pH 9) and EDTA to 500 µL of sample. Then, 500 µL of FMOC (fluorenemethoxycarbonyle) are added and the samples were shaked during 20 minutes. Finally, 100 µL of orthophosphoric acid were added to stop the reaction. The samples were shaked for 1 minutes before LC-MS injection for quantification.

Table S4. Gradient of solvents used for LC-MS-MS quantification of A) cyazofamid (CYA), cyprodinil (CYP), difenoconazole (DIF), kresoxim methyl (KM), metalaxyl (MET), pyrimethanil (PYR), spiroxamine (SPI), teraconazole (TET), B) fludioxonil (FLU), C) glyphosate (GLY) and Aminomethylphosphonic acid (AMPA).

A)

Positive mode (CYA, CYP, DIF, KM, MET, PYR, SPI, TET)			
Time (min)	Flow (µl/min)	% pure water	% acetonitrile
0	350	100	0
0.5	350	70	30
15	350	30	70
16	350	0	100
18	350	0	100
18.1	350	100	0
30	350	100	0

B)

Negative mode (FLU)			
Time (min)	Flow (µl/min)	% pure water	% acetonitrile
0	400	100	0
4	400	5	95
6	400	0	100
9	400	0	100
9.1	400	100	0
16	400	100	0

C)

Negative mode (GLY, AMPA)			
Time (min)	Flow (µl/min)	% acetate buffer	% acetonitrile
0	400	100	0
2	400	85	15
7	400	10	90
8	400	0	100
10	400	0	100
10,1	400	100	0
20	400	100	0

Table S5. Calculation of pesticide loads in the compartments of the stormwater wetland (Rouffach, Alsace, France), accounting for the monthly pesticide mass budget and associated errors.

Wetland compartment	Wetland location	Pesticide load calculation	Errors calculation *via* error propagation
Dissolved phase (DISS)	Inlet, outlet, forebay, gravel filter	$Cpest_{DISS} \times V_{water\ compartment}$	$Cpest_{DISS}$ ± 21 to 27% (see Table S2) $V_{water\ compartment}$ ± 5%
TSS	Inlet, outlet, forebay, gravel filter	$Cpest_{TSS} \times C_{TSS} \times V_{water\ compartment}$	$Cpest_{TSS}$ ± 26 to 45% (see Table S2) $V_{water\ compartment}$ ± 5% C_{TSS} ± 0.1 to 12.5%
Macroinvertebrates (MI)	Forebay	$Cpest_{MI} \times M_{MI\text{-}COLLECTED} \times Area_{WETLAND}$	$Cpest_{DISS}$ ± 21 to 43% (see Table S2) $M_{MI\text{-}COLLECTED}$ ± 5%
Algae (Alg)	Forebay	$Cpest_{Alg} \times M_{Alg\text{-}COLLECTED} \times V_{FOREBAY}$	$Cpest_{DISS}$ ± 21 to 43% (see Table S2) $M_{Alg\text{-}COLLECTED}$ ± 5%
Phragmites roots and aerial parts	Forebay	$Cpest_{Phrag} \times M_{Phrag\text{-}COLLECTED} \times Density_{Phrag} \times Area_{WETLAND}$	$Cpest_{DISS}$ ± 21 to 43% (see Table S2) $M_{Phrag\text{-}COLLECTED}$ ± 0.1% $Density_{Phrag}$ ± 10%
Bed sediments (50-250 µm; 250-1000 µm and >1000 µm)	Forebay	$Cpest_{SED} \times M_{SED\text{-}COLLECTED} \times Area_{WETLAND}$	$Cpest_{DISS}$ ± 26 to 45% (see Table S2) $M_{SED\text{-}COLLECTED}$ ± 10%

Cpest denotes the pesticide concentrations in the dissolved phase (DISS), the total suspended solids (TSS), the macroinvertebrates (MI), the algae (Alg.), The Phragmites roots or aerial parts (Phrag.) or the different fractions of bed sediments (SED). $V_{water\ compartment}$ represents the water volumes respectively at the inlet, outlet, in the forebay and in the gravel filter. C_{TSS} represents the concentration of TSS measured at the inlet, the outlet, the forebay and the gravel filter. M is the (bio)mass of the different wetland compartments. $Density_{Phrag.}$ is the plant density [stems m^{-2}] of *Phragmites australis*.

Table S6. Weekly concentrations of Total Suspended Solids (TSS), Particulate Organic Carbon (POC) and organic carbon content measured at the inlet, outlet and in the forebay during the investigation period (from March 23, 2011 to September 28, 2011).

	INLET					WETLAND FOREBAY					OUTLET				
	TSS	TOC	DOC	POC	% OC	TSS	TOC	DOC	POC	% OC	TSS	TOC	DOC	POC	% OC
Date	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[%]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[%]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[%]
3/23/2011	n.a.	n.a.	n.a.	n.a.	n.a.	172	3.73	3.70	n.a.	0.01	173	4.12	4.07	n.a.	n.a.
3/30/2011	n.a.	n.a.	n.a.	n.a.	n.a.	1.6	4.46	4.70	n.a.	n.a.	13.3	4.92	4.89	n.a.	n.a.
04/06/2011	n.a.	n.a.	n.a.	n.a.	n.a.	5.3	7.09	6.47	0.62	11.74	6.1	6.58	5.99	0.59	9.54
4/13/2011	n.a.	n.a.	n.a.	n.a.	n.a.	14.5	9.76	8.20	1.56	10.75	5.4	7.65	6.28	1.37	25.35
4/20/2011	n.a.	n.a.	n.a.	n.a.	n.a.	20.8	7.26	6.37	0.89	4.29	96.4	4.65	5.20	n.a.	n.a.
4/27/2011	n.a.	n.a.	n.a.	n.a.	n.a.	1.8	7.68	7.50	0.18	10.22	36.8	5.54	5.58	n.a.	n.a.
05/04/2011	430	60.48	41.17	19.31	4.49	11.7	7.78	6.36	1.42	12.21	11.9	5.6	4.63	0.97	8.15
05/11/2011	112	47.94	n.a.	n.a.	n.a.	19.7	11.59	10.09	1.50	7.63	47.2	9.97	8.79	1.18	2.49
5/18/2011	497	24.60	24.47	0.13	0.03	3.5	8.94	8.29	0.65	18.57	13.6	6.41	6.60	n.a.	n.a.
5/25/2011	5972	45.12	17.34	27.78	0.47	16.0	n.a.	n.a.	n.a.	n.a.	19.6	9.64	9.41	0.23	1.18
06/01/2011	548	25.96	28.30	n.a.	n.a.	6.4	11.47	13.10	n.a.	n.a.	44.0	8.57	10.60	n.a.	n.a.
06/08/2011	110	30.32	35.11	n.a.	n.a.	4.3	11.04	12.22	n.a.	n.a.	4.9	n.a.	n.a.	n.a.	n.a.
6/15/2011	1614	30.16	19.95	10.21	0.63	4.8	10.2	9.97	0.23	4.75	25.6	n.a.	n.a.	n.a.	n.a.
6/22/2011	620	24.09	17.01	7.08	1.14	13.4	10.12	10.96	n.a.	n.a.	26.0	8.10	8.50	n.a.	n.a.
6/29/2011	2866	34.33	18.6	15.73	0.55	36.0	9.72	10.29	n.a.	n.a.	69.8	8.06	8.59	n.a.	n.a.
07/06/2011	660	11.63	10.15	1.48	0.22	24.6	12.24	12.41	n.a.	n.a.	20.5	10.37	10.28	n.a.	n.a.
07/12/2011	655	16.99	13.52	3.47	0.53	4.6	7.24	6.78	0.46	9.89	17.8	7.73	8.70	n.a.	n.a.
7/20/2011	389	20.28	15.08	5.20	1.34	6.6	11.01	10.55	0.46	6.95	3.4	7.35	7.16	0.19	5.41
7/27/2011	1150	21.57	22.85	n.a.	n.a.	18.0	8.2	7.90	0.30	1.63	14.3	6.95	7.97	n.a.	n.a.
08/03/2011	98.6	37.74	38.77	n.a.	n.a.	7.6	13.67	13.51	0.16	2.11	4.9	8.52	8.98	n.a.	n.a.
08/10/2011	494	22.49	22.75	n.a.	n.a.	2.6	10.27	10.04	0.23	8.77	9.0	8.91	8.37	0.54	5.96
8/17/2011	22.5	19.57	21.62	n.a.	n.a.	8.6	13.27	13.01	0.26	3.06	2.5	23.45	23.07	0.38	15.24
8/24/2011	43.3	35.90	37.12	n.a.	n.a.	13.2	13.12	13.58	n.a.	n.a.	3.8	8.66	8.78	n.a.	n.a.
8/31/2011	551	16.02	17.77	n.a.	n.a.	18.2	11.48	11.41	n.a.	n.a.	14.8	10.71	10.55	0.16	1.11
09/07/2011	39.0	14.09	15.06	n.a.	n.a.	7.0	11.55	11.63	n.a.	n.a.	6	8.70	8.29	0.41	6.87
9/14/2011	392	14.89	17.32	n.a.	n.a.	4.0	12.11	11.96	0.15	3.82	2.6	8.67	8.54	0.13	5.12
9/21/2011	n.a.	n.a.	n.a.	n.a.	n.a.	2.0	11.2	10.10	1.10	55	3.3	8.90	8.60	0.30	9.09
9/28/2011	n.a.	n.a.	n.a.	n.a.	n.a.	24.0	11.3	11.70	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Pesticide partitioning in the runoff. The runoff volume entering the wetland during the investigation period was 1,944 m^3. The input of the TSS was 2.3 tons and that of dissolved organic carbon (DOC) was 36.1 kg. Ninety-five percent of the total pesticide load detected at the inlet of the wetland was found in the dissolved phase of the runoff (< 0.7 µm). The low amount of solid-bound pesticides reflects the effect of grass cover on the vineyard plots, which may significantly reduce erosion and solid transport. The maximum rainfall intensities significantly correlated on a weekly basis with the TSS and the total pesticide loads (i.e dissolved and solid-bound loads) entering the wetland ($p < 0.05$). However, the rainfall intensity did not affect the export of solid-bound pesticides in the runoff from the vineyard catchment, as indicated by the absence of a correlation between the rainfall intensities and the solid-bound pesticide loads.

Four groups of pesticides could be distinguished according to their partitioning in runoff water. The first group consisted of the dithiocarbamates, cyprodinil and difenoconazole, which were exclusively associated with the TSS and were not found in the dissolved phase (< 0.7 µm). The second group, composed of kresoxim-methyl, pyrimethanil, metalaxyl and tetraconazole was mostly detected in the dissolved phases, underscoring their predominant occurrence in the aqueous phase, possibly in association with colloids < 0.22 µm. Glyphosate, AMPA, fludioxonil and spiroxamine composed the third group and were found in all three fractions, but mainly in the dissolved phases. Finally, cyazofamid was found in filtrates < 0.7 µm but never in those < 0.22 µm, indicating its transport on dissolved organic or mineral materials ranging from 0.22 µm to 0.7 µm. Our results underline that both dissolved and solid-bound pesticides should be considered when evaluating pesticide transport and dissipation in wetland systems.

The octanol-water partition coefficient (log K_{ow}) and the distribution coefficient (K_d) are commonly used to estimate pesticide sorption and environmental risks. In our study, no significant relationship could be found between phase partitioning of pesticides and the lab-defined log K_{ow} values ($p > 0.05$). Despite the relatively low log K_{ow} values for dithiocarbamates (1.3 for mancozeb, and 1.76 for metiram-zinc), the dithiocarbamates were exclusively associated with TSS. In contrast, the hydrophobic cyazofamid and kresoxim methyl were only measured in the dissolved phases (Figure 2, Table S2).

The solids-to-water ratios (K_d) and the organic carbon partition coefficients (K_{oc}) at the inlet, outlet and in the forebay are provided in Table S7 in the supplementary information. The K_d values were determined experimentally and was calculated according to the following equation:

$$K_d = \frac{C_{TSS}}{C_{diss}} \qquad \text{(eq. S3)}$$

where C_{TSS} (mg kg^{-1}) is the pesticide concentration in the total suspended solids and C_{diss} (mg L^{-1}) is the pesticide concentration in the dissolved phase. The K_d values (L kg^{-1}) were calculated only for samples in which both C_{TSS} and C_{diss} were above the quantification limits.

The partition coefficients were normalized for samples that had available particulate organic carbon data (POC) using the following formula:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{(eq. S4)}$$

where f_{oc} is the ratio of POC to TSS per liter of water and where POC was calculated as the difference between the Total Organic Carbon (TOC, in mg L^{-1}) and the Dissolved Organic Carbon (DOC, in mg L^{-1}) concentrations.

The average K_d values observed at the inlet of the stormwater wetland for glyphosate were in the range of those retrieved from the literature.

For most pesticides, no significant correlation could be observed between the concentrations of TSS or DOC and pesticides at the wetland inlet and outlet and in the forebay.

However, the DOC concentrations positively correlated with glyphosate and AMPA during the spring ($p < 0.005$), which is in agreement with previous observations showing that 40% of the amount of glyphosate in a sandy soil was associated with humic and fulvic acids (Albers et al., 2009).

Reference:

Albers, C.N.; Banta, G.T.; Hansen, P.E.; Jacobsen, O.S., The influence of organic matter on sorption and fate of glyphosate in soil – Comparing different soils and humic substances. *Environ Pollut* **2009**, *157*, (10), 2865-2870.

Table S7. Apparent partitioning coefficients (K_d) (C_{TSS}/C_{diss}) [L kg^{-1}] and organic carbon partition coefficients (K_{oc}) (K_d/f_{oc}) for pesticides at the inlet, in the forebay and at the outlet of the stormwater wetland (Rouffach, Alsace, France). The values represent the mean (min-max.) of *n* measurement for which both pesticides and TSS (and organic carbon content) concentrations were above the quantification limits.

	INLET				FOREBAY				OUTLET			
Compound	K_d	*n*	K_{oc}	*n*	K_d	*n*	K_{oc}	*n*	K_d	*n*	K_{oc}	*n*
Glyphosate	87.06 (2.5 - 228.6)	17	7786.6 (569.7 - 17841)	7	4490 (120 - 22000)	19	170048 (1885 - 719392)	9	18067 (312 - 65000)	11	565701 (109223 - 1255757)	5
AMPA	229.3 (1.4 - 1571.4)	18	7754.5 (178.2 - 21892.6)	8	2020 (135 - 7143)	18	97633 (2621 - 342857)	9	3787 (812 - 13750)	8	112852 (44876 - 230876)	3
Cymoxanil	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Dithiocarbamates	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Kresoxim methyl	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Pyrimethanil	833.3 (666.7 - 1000)	2	n.a.	-	n.a.	-	n.a.	-	414 (77 - 1000)	3	15870 (14949 - 16791)	2
Metalaxyl	n.a.		n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Tetraconazole	524.8 (407.7 - 666.7)	3	n.a.	-	583 (333 - 1000)	6	13678 (1212 - 26143)	2	1533 (500 - 4666)	5	40409 (11000 - 91228)	4
Difenoconazole	n.a.		n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Fludioxonil	944.4 (333.3 - 1500)	3	n.a.	-	944 (476 - 1500)	6	16198 (1272 - 31123)	2	977 (280 - 2416)	5	21737 (6107 - 47243)	4
Spiroxamine	1461 (166.7 - 6000)	10	50584.7 (17615.4 - 107714.9)	5	1102 (280 - 1786)	6	32467 (9978 - 84821)	5	1681 (642 - 3400)	3	18478	1
Cyprodinil	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Cyafozamid	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-

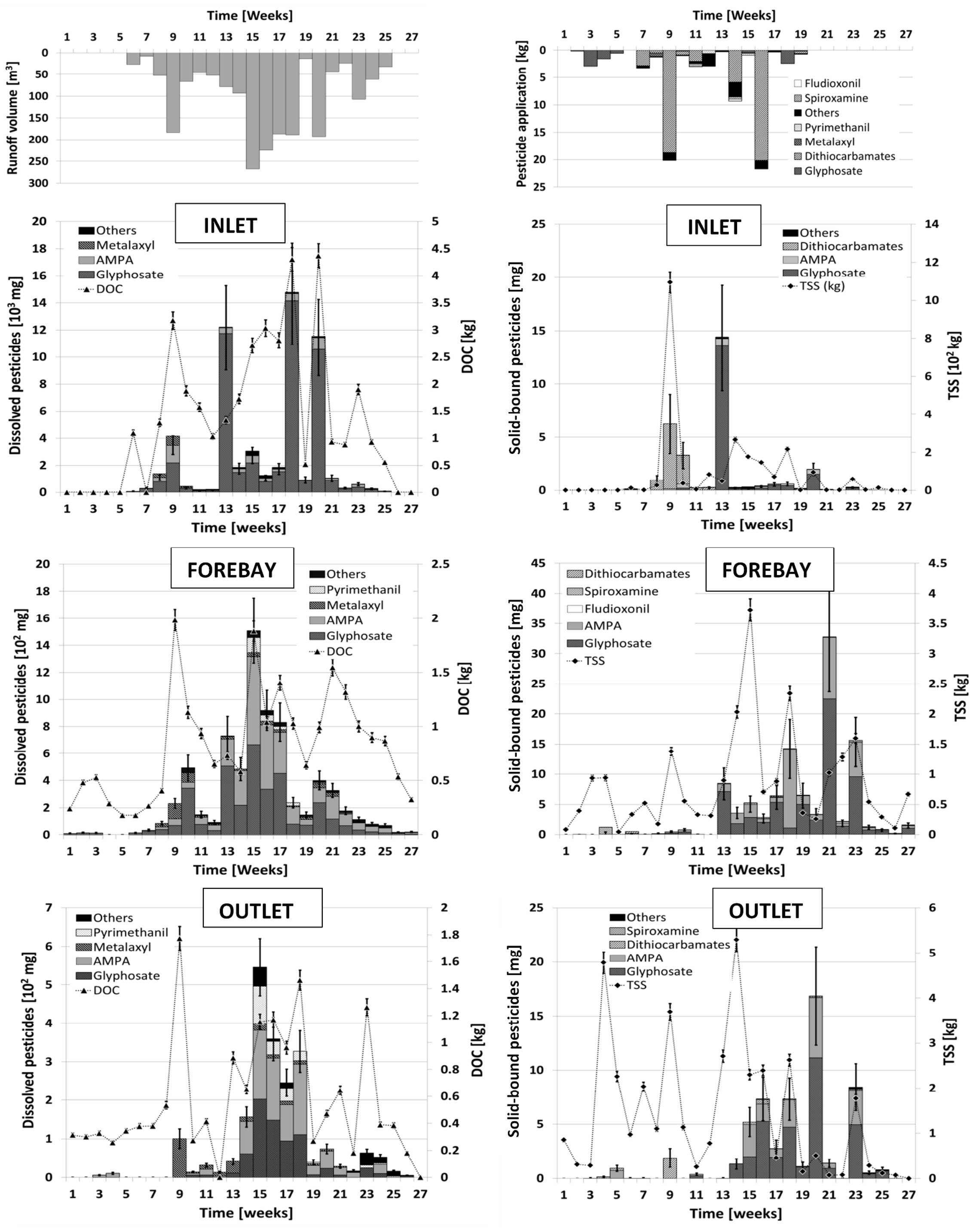

Figure S1. Loads of dissolved (<0.7 µm; on the left) and solid-bound (>0.7 µm; on the right) pesticides at the inlet, in the forebay and at the outlet of the stormwater wetland (Rouffach, Alsace, France). Error bars correspond to the analytical uncertainty. Errors for total pesticide loads were calculated by error propagation, incorporating analytical uncertainties of individual pesticide concentration measurements as well as the uncertainty of water volume measurement

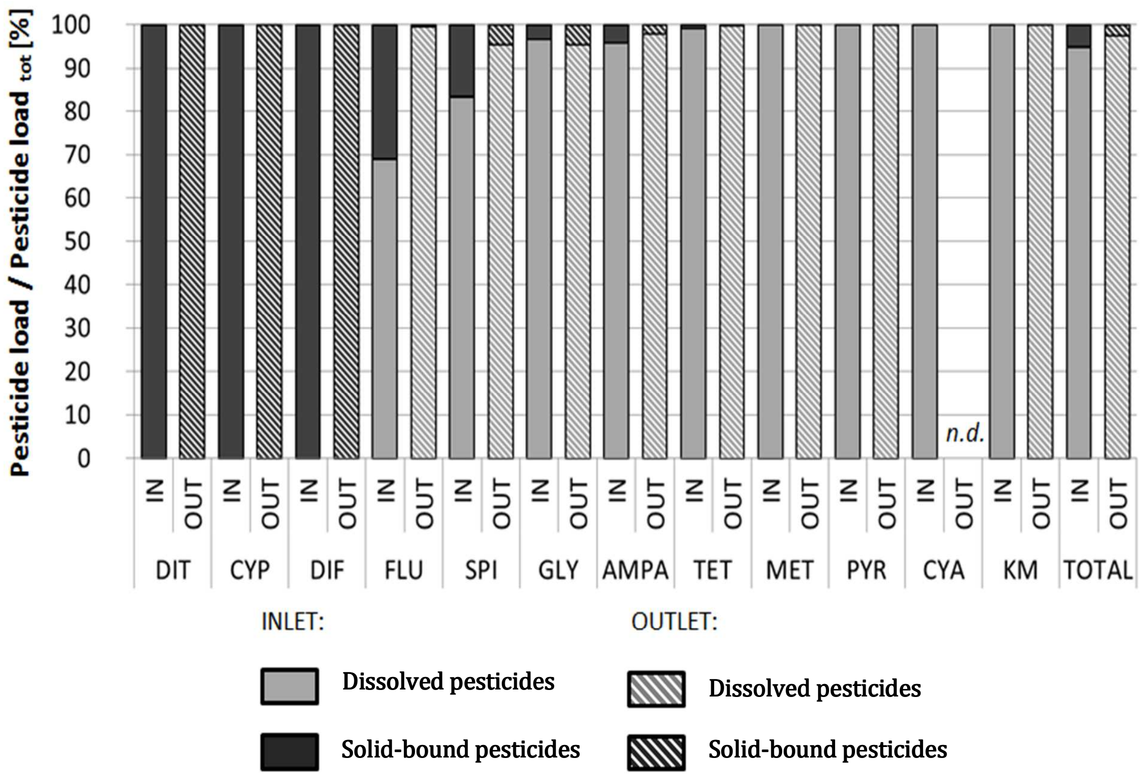

Figure S2. Relative loads of solid-bound (> 0.7 µm) and dissolved (< 0.7 µm) pesticides at the inlet and the outlet of the stormwater wetland (Rouffach, Alsace, France). *n.d.* = not detected. DIT: dithiocarbamates, CYP: cyprodinil, DIF: difenoconazole, FLU: fludioxonil, SPI: spiroxamine, GLY: glyphosate, AMPA: Aminomethyl phosphonic acid, TET: tetraconazole, MET: metalaxyl, PYR: pyrimethanil, CYA: cyazofamid, and KM: kresoxim-methyl.

Pesticide mass budget calculations. The dissolved and solid-bound loads for a pesticide X degraded monthly in the stormwater wetland (Rouffach, Alsace, France) was calculated according to Eq. S1, as follows:

$$
\begin{aligned}
Degraded\ load_X &= \sum_{t=1}^{4}\left[V_{In,t}\ (Conc_{In\ DISS,t}^{X} + \left(Conc_{In\ TSS,t} \times Conc_{In\ TSS,t}^{X}\right))\right] \\
&- \sum_{i=1}^{4}\left[V_{Out,t}\left(Conc_{Out\ DISS,t}^{X} + \left(Conc_{Out\ TSS,t} \times Conc_{Out\ TSS,t}^{X}\right)\right)\right] \\
&- \left[\sum_{i=1}^{7}\left(Conc_{i}^{X} \times M_i\right)\right. \\
&+ V_{Forb}\left(Conc_{Forb\ DISS}^{X} + \left(Conc_{Forb\ TSS} \times Conc_{Forb\ TSS}^{X}\right)\right) \\
&\left.+ V_{Filter}\left(Conc_{Filter\ DISS}^{X} + \left(Conc_{Filter\ TSS} \times Conc_{Filter\ TSS}^{X}\right)\right)\right] \qquad \text{(S1)}
\end{aligned}
$$

where $V_{In,t}$ denotes the inlet water volume and $V_{Out,t}$ the outlet water volume; $Conc_{In\ TSS,t}$ and $Conc_{Out\ TSS,t}$ are the TSS concentrations measured in the week t respectively at the inlet and the outlet of the wetland; and $Conc_{In\ DISS,t}^{X}$, $Conc_{Out\ DISS,t}^{X}$, $Conc_{In\ TSS,t}^{X}$ and $Conc_{Out\ TSS,t}^{X}$ represent the concentration of the pesticide X measured in the week t in the dissolved phase (<0.7 µm) and in TSS at the wetland inlet and outlet respectively. The pesticide load in each wetland compartment was estimated monthly by multiplying the pesticide concentration in each wetland compartment by the corresponding (bio)mass or volume of the compartment (Table S5). $Conc_{i}^{X}$ represents the pesticide concentration and M_i the (bio)mass of the 7 wetland compartments *i*, i.e. algae, *Phragmites* roots, *Phragmites* aerial parts, invertebrates, bed sediments 50-250 µm, bed sediments 250 µm–1000 µm and bed sediments >1000 µm. Pesticide loads stored in the forebay and the gravel filter water were calculated as the sum of the dissolved and the solid-bound loads where V_{Forb} and V_{Filter} are the water volumes stored in the forebay and the gravel filter respectively; $Conc_{Forb\ TSS}$ and $Conc_{Filter\ TSS}$ represent the TSS concentrations measured in the forebay and in the gravel filter respectively; and $Conc_{Forb\ DISS}^{X}$, $Conc_{Forb\ TSS}^{X}$, $Conc_{Filter\ DISS}^{X}$, and $Conc_{Filter\ TSS}^{X}$ are the concentrations of the pesticide X measured monthly in the dissolved phase and the TSS in the forebay and in the gravel filter.

The temporal changes in the pesticide stocks accounting for all wetland compartments were calculated according to eq. S2, as follows:

$$\Delta\ Load\ STORED = Load\ STORED_{month_{m+1}} - Load\ STORED_{month_{m}} \qquad \text{(S2)}$$

Δ *Load STORED* < 0 indicates pesticide degradation or release by the wetland, and Δ *Load STORED* > 0 indicates pesticide storage in the wetland compartments.

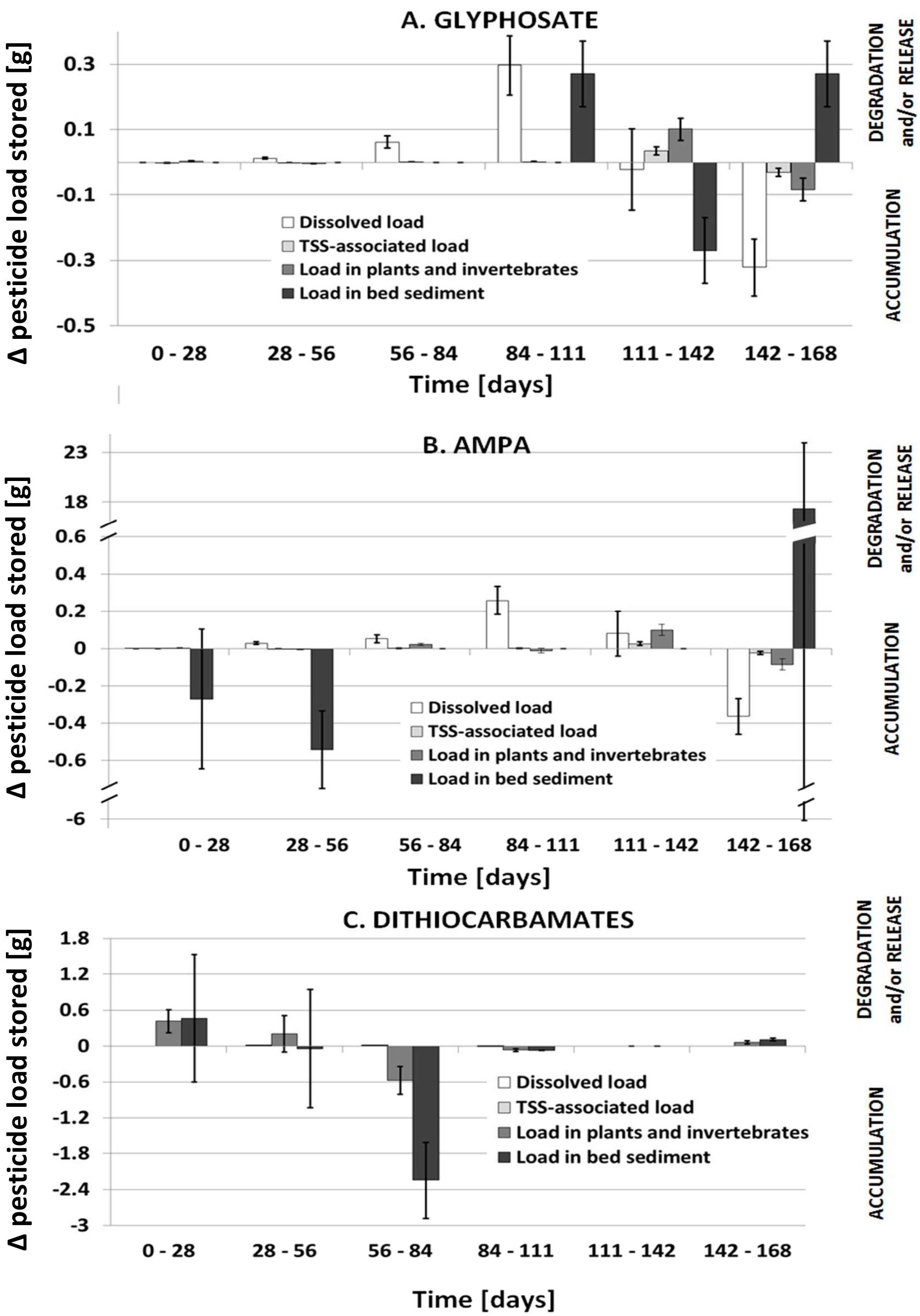

Figure S3. Temporal changes in the pesticide loads stored in the stormwater wetland (Rouffach, Alsace, France) for glyphosate (A), AMPA (B) and dithiocarbamates (C). Days 0, 28, 56, 84, 111, 142 and 168 correspond to the monthly sampling campaigns (i.e. March 23th, April 20th, May 18th, June 15th, July 12th, August 10th and September 7th, 2011). The error given for the pesticide loads in each wetland compartment at the sampling time was calculated *via* error propagation based on the uncertainty of the pesticide concentration measurements and the mass estimate for each compartment (Table S5).

Table S8. Hydrochemistry at the inlet, the outlet and in the forebay of the stormwater wetland (Rouffach, Alsace, France) during the periods 0-56, 56-142 and 142-168 days. Analytical uncertainties were 5% for major ions, metals and carbon concentrations. Precision was ± 0.5% for conductivity and dissolved oxygen measurements, ± 0.01 unit for pH and ± 10 mV for redox potential. D.O., TOC, DOC and E.C. represent, respectively, the concentrations of dissolved oxygen, total organic carbon, dissolved organic carbon and the electrical conductivity. The values represent the mean ± 2s.

		Day 0 - Day 56			Day 56 - Day 142			Day 142 - Day 168		
Parameter	**Unit**	**INLET**	**FOREBAY**	**OUTLET**	**INLET**	**FOREBAY**	**OUTLET**	**INLET**	**FOREBAY**	**OUTLET**
D.O. [a]	ppm	n.a.	3.86 ± 4.09	n.a.	n.a.	0.28 ± 0.27	n.a.	n.a.	0.21 ± 0.19	n.a.
Redox [a]	mV	n.a.	47 ± 160	n.a.	n.a.	-44 ± 35	n.a.	n.a.	n.a.	n.a.
pH [a]	-	n.a.	7.34 ± 0.29	n.a.	n.a.	7.08 ± 0.26	n.a.	n.a.	7.03 ± 0.16	n.a.
E.C. [a]	$\mu S\ cm^{-1}$	n.a.	925 ± 130	n.a.	n.a.	513 ± 106	n.a.	n.a.	448 ± 44	n.a.
Temp. [a]	°C	n.a.	11.93 ± 2.54	n.a.	n.a.	16.93 ± 1.75	n.a.	n.a.	15.475 ± 0.10	n.a.
TOC [b]	ppm	44.34 ± 18.21	7.59 ± 2.44	6.16 ± 1.79	26.72 ± 9.33	10.47 ± 1.77	8.42 ± 1.03	21.40 ± 9.93	12.35 ± 0.97	12.88 ± 7.11
DOC [b]	ppm	32.82 ± 11.81	6.85 ± 1.93	5.78 ± 1.39	21.62 ± 8.61	10.70 ± 2.08	8.85 ± 1.03	22.89 ± 9.86	12.41 ± 1.05	12.67 ± 7.00
$\mathbf{Al^{3+}}$ [b]	ppm	0.08 ± 0.05	0.04 ± 0.01	0.04 ± 0.03	0.17 ± 0.11	0.04 ± 0.03	0.03 ± 0.01	0.07 ± 0.04	0.04 ± 0.02	0.05 ± 0.08
$\mathbf{Fe^{3+}}$ [b]	ppm	0.10 ± 0.09	0.02 ± 0.03	0.01 ± 0.02	0.21 ± 0.14	0.12 ± 0.11	0.09 ± 0.06	0.15 ± 0.05	0.16 ± 0.05	0.54 ± 0.98
$\mathbf{Fe^{2+}}$ [b]	ppm	0.80 ± 0.94	0.03 ± 0.05	0.04 ± 0.06	0.51 ± 0.81	0.19 ± 0.19	0.21 ± 0.16	0.09 ± 0.07	0.09 ± 0.04	0.04 ± 0.03
$\mathbf{Cu^{2+}}$ [b]	ppb	23.14 ± 13.17	6.40 ± 1.86	7.04 ± 2.72	36.59 ± 19.62	8.00 ± 3.46	5.84 ± 3.41	34.03 ± 13.17	5.41 ± 2.00	3.79 ± 3.64
$\mathbf{SO_4^{2-}}$ [b]	ppm	77.92 ± 103.06	221.49 ± 19.38	209.29 ± 22.14	8.68 ± 3.07	55.55 ± 71.94	36.20 ± 46.62	5.58 ± 2.85	3.52 ± 2.54	4.17 ± 2.6
$\mathbf{NO_2^{-}}$ [b]	ppm	0.36 ± 0.21	0.17 ± 0.08	0.11 ± 0.09	0.1 ± 0.11	0.10 ± 0.14	0.09 ± 0.14	0.04 ± 0.08	0.03 ± 0.06	0.04 ± 0.07
$\mathbf{NO_3^{-}}$ [b]	ppm	0.99 ± 0.39	3.23 ± 2.74	1.57 ± 1.55	0.92 ± 0.77	0.41 ± 0.48	0.96 ± 0.15	0.3 ± 0.61	0.45 ± 0.31	0.46 ± 0.56
$\mathbf{NH_4^{+}}$ [b]	ppm	0.16 ± 0.09	n.d.	n.d.	0.09 ± 0.06	0.07 ± 0.15	0.04 ± 0.06	0.03 ± 0.05	n.d.	n.d.
$\mathbf{PO_4^{3-}}$ [b]	ppm P	0.43 ± 0.03	0.41 ± 0.03	0.42 ± 0.04	0.64 ± 0.12	0.57 ± 0.18	0.55 ± 0.17	0.53 ± 0.21	0.39 ± 0.02	0.36 ± 0.03

[a] Mean values were calculated on the basis of data collected monthly.
[b] Mean values were calculated on the basis of data collected weekly.