

Supplementary Materials: Transfer Pathways and Fluxes of Water-Soluble Pesticides in Various Compartments of the Agricultural Catchment of the Canche River (Northern France)

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Table S1. GPS coordinates of sampling sites.

river/site	longitude	latitude
Canche 0	50°22'43.1"N	2°01'03.5"E
Ternoise	50°22'47.6"N	2°02'33.7"E
Canche 1	50°23'09.0"N	1°59'59.6"E
Planquette	50°24'26.0"N	1°58'11.0"E
Canche 2	50°24'45.5"N	1°55'43.3"E
Créquoise	50°25'49.5"N	1°54'23.2"E
Canche 3	50°25'57.2"N	1°53'37.6"E
Bras de Bronne	50°27'22.0"N	1°49'32.6"E
Canche 4	50°27'32.0"N	1°47'58.7"E
Course	50°28'50.7"N	1°45'51.9"E
Canche 5	50°28'41.1"N	1°44'55.9"E
Dordogne	50°30'01.4"N	1°42'28.4"E
Canche 6	50°29'39.5"N	1°41'11.8"E
Huîtrepin	50°30'15.6"N	1°41'30.5"E
Canche 7	50°30'10.8"N	1°40'24.4"E

Table S2. Dissolved concentrations of pesticides during the seasonal campaign (ng L⁻¹).

		Ternoise	Planquette	Créquoise	Bras de Bronne	Course	Dordogne	Huîtrepin	Canche 0	Canche 1	Canche 2	Canche 3	Canche 4	Canche 5	Canche 6	Canche 7
February 16	atrazine	11	10	10	13	18	17	16	8	9	9	8	10	12	12	11
	diflufenican	3	3	1	2	2	9	3	2	3	2	2	2	2	3	3
	ethofumesathe	<1	<1	<1	<1	<1	2	2	<1	<1	<1	<1	<1	<1	1	1
	metolachlor	1	3	1	1	2	1	2	1	1	1	1	1	1	2	2
	pendimethalin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
May 16	atrazine	14	13	13	19	21	19	19	11	13	13	13	11	10	11	11
	diflufenican	2	2	2	2	4	8	4	2	2	2	3	3	3	3	3
	ethofumesathe	27	8	37	10	25	3	6	7	11	12	14	11	8	10	12
	metolachlor	5	6	352	3	3	2	41	3	5	6	39	33	22	20	15
	pendimethalin	<1	<1	<1	<1	<1	1	1	5	2	2	2	2	2	1	1
July 16	atrazine	13	11	11	17	16	15	16	10	13	11	11	12	12	12	13
	diflufenican	<1	1	<1	1	1	2	2	1	1	1	1	1	1	1	1
	ethofumesathe	1	<1	<1	<1	<1	1	1	1	<1	<1	1	1	1	1	1
	metolachlor	7	2	2	5	2	1	2	3	3	3	2	4	3	2	2
	pendimethalin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
November 16	atrazine	13	9	9	10	14	9	11	9	11	10	8	7	10	12	12
	diflufenican	3	34	5	21	4	52	25	9	5	7	4	5	4	7	9
	ethofumesathe	<1	<1	<1	3	<1	6	2	<1	<1	<1	<1	<1	<1	<1	<1
	metolachlor	<1	2	<1	2	1	4	4	2	<1	<1	<1	<1	1	1	5
	pendimethalin	4	5	24	28	18	101	27	3	3	4	5	7	9	13	11

Table S3. Herbicides fluxes calculated during the seasonal campaigns (g day⁻¹).

		Terroise	Planquette	Créquoise	Bras deBrône	Course	Dordogne	Huîtrepin	Canche 0	Canche 1	Canche 2	Canche 3	Canche 4	Canche 5	Canche 6	Canche 7
February 16	Water discharge (m ³ s ⁻¹)	7	1	2	2	6	2	2	9	16	17	19	20	26	28	29
	atrazine	6.6	1.0	1.4	1.8	8.5	3.0	2.2	6.1	12.2	12.9	12.4	17.9	27.2	28.0	28.2
	diflufenican	1.7	0.3	0.1	0.3	1.0	1.5	0.4	1.9	3.7	3.6	3.8	4.1	4.4	7.1	7.5
	ethofumesathe	<0.2	<0.1	<0.1	<0.2	<0.2	0.4	0.2	<0.3	<0.5	<0.5	<0.5	<0.6	<0.8	1.3	1.3
	metolachlor	0.7	0.3	0.1	0.2	0.9	0.2	0.2	0.7	1.3	1.6	2.0	2.1	2.9	4.1	4.0
	pendimethalin	<0.2	<0.1	<0.1	<0.2	<0.2	<0.2	<0.2	<0.3	<0.5	<0.5	<0.5	<0.6	<0.8	<0.8	<0.9
May 16	Water discharge (m ³ s ⁻¹)	5	1	1	1	4	1	1	7	13	13	15	16	20	21	22
	atrazine	6.5	1.0	1.4	1.8	6.6	2.2	1.7	6.6	14.4	15.1	16.0	15.5	16.5	19.8	21.0
	diflufenican	1.1	0.1	0.2	0.2	1.2	0.9	0.3	1.4	2.7	2.6	3.3	3.6	4.3	5.4	5.7
	ethofumesathe	12.3	0.6	4.0	1.0	7.7	0.3	0.6	4.6	12.2	13.4	17.5	15.1	13.8	18.1	22.7
	metolachlor	2.2	0.4	37.7	0.3	0.9	0.2	3.7	1.8	5.3	7.0	50.1	45.6	37.3	36.2	28.5
	pendimethalin	<0.2	<0.1	<0.1	<0.2	<0.2	0.1	0.8	2.9	1.9	2.3	2.5	2.8	3.4	1.8	2.1
July 16	Water discharge (m ³ s ⁻¹)	5	1	1	1	3	1	1	5	10	11	12	13	16	17	18
	atrazine	5.2	0.8	1.0	1.3	4.2	1.3	1.1	4.7	11.1	10.0	11.4	13.0	15.9	17.8	20.0
	diflufenican	<0.2	<0.1	<0.1	0.1	0.2	0.2	0.1	0.5	0.5	0.5	0.6	0.7	1.0	0.9	1.0
	ethofumesathe	0.2	<0.1	<0.1	<0.2	<0.2	0.1	0.8	0.3	<0.5	<0.5	0.5	0.6	1.0	0.8	0.9
	metolachlor	2.7	0.1	0.2	0.4	0.4	0.1	0.1	1.3	2.6	2.7	2.4	4.5	4.7	2.9	2.3
	pendimethalin	<0.2	<0.1	<0.1	<0.2	<0.2	<0.2	<0.2	<0.3	<0.5	<0.5	<0.5	<0.6	<0.8	<0.8	<0.9
November 16	Water discharge (m ³ s ⁻¹)	4	1	1	1	2	1	1	5	8	9	10	11	13	14	14
	atrazine	4.1	0.5	0.7	0.6	2.8	0.6	0.6	3.8	7.8	8.0	6.8	6.5	10.9	14.1	15.3
	diflufenican	1.1	1.8	0.4	1.3	0.8	3.7	1.4	3.5	3.4	5.1	3.5	4.4	4.7	7.7	11.3
	ethofumesathe	<0.2	<0.1	<0.1	0.2	<0.2	0.4	0.1	<0.3	<0.5	<0.5	<0.5	<0.6	<0.8	<0.8	<0.9
	metolachlor	<0.2	0.1	<0.1	0.1	0.3	0.3	0.2	0.7	<0.5	<0.5	<0.5	<0.6	0.9	1.0	6.3
	pendimethalin	1.3	0.3	1.8	1.7	3.6	7.2	1.5	1.3	2.5	2.9	4.7	5.9	10.0	14.8	14.2

Table S4. Mass balance analysis: agreement between the tributaries and the closest effluent point (%).

		Canche 1	Canche 2	Canche 3	Canche 4	Canche 5	Canche 6	Canche 7
February 16	atrazine	103 ± 33	102 ± 32	114 ± 36	79 ± 25	96 ± 31	107 ± 34	107 ± 34
	diiflufenican	97 ± 31	108 ± 34	97 ± 31	102 ± 32	114 ± 36	84 ± 27	100 ± 32
	ethofumesathe	-	-	-	-	-	31 ± 10	116 ± 37
	metolachlor	111 ± 35	103 ± 33	88 ± 28	101 ± 32	105 ± 33	76 ± 24	107 ± 34
	pendimethalin	-	-	-	-	-	-	-
May 16	atrazine	90 ± 29	102 ± 32	102 ± 32	115 ± 36	133 ± 42	94 ± 30	102 ± 32
	diiflufenican	94 ± 30	109 ± 34	82 ± 26	98 ± 31	109 ± 35	96 ± 30	101 ± 32
	ethofumesathe	138 ± 44	94 ± 30	99 ± 31	121 ± 39	166 ± 53	77 ± 24	82 ± 26
	metolachlor	74 ± 23	83 ± 26	89 ± 28	110 ± 35	124 ± 39	103 ± 33	139 ± 44
	pendimethalin	146 ± 47	84 ± 27	90 ± 28	91 ± 29	81 ± 26	195 ± 62	87 ± 28
July 16	atrazine	89 ± 28	118 ± 37	97 ± 31	97 ± 31	108 ± 34	96 ± 31	94 ± 30
	diiflufenican	89 ± 28	108 ± 34	84 ± 26	94 ± 30	91 ± 29	119 ± 38	102 ± 32
	ethofumesathe	-	-	-	86 ± 27	62 ± 19	135 ± 43	93 ± 29
	metolachlor	154 ± 49	101 ± 32	122 ± 39	62 ± 19	103 ± 33	166 ± 53	132 ± 42
	pendimethalin	-	-	-	-	-	-	-
November 16	atrazine	101 ± 32	103 ± 32	128 ± 41	112 ± 35	85 ± 27	81 ± 26	95 ± 30
	diiflufenican	133 ± 42	102 ± 32	158 ± 50	108 ± 34	109 ± 35	108 ± 34	81 ± 25
	ethofumesathe	-	-	-	-	-	-	-
	metolachlor	-	-	-	-	-	118 ± 38	18 ± 5
	pendimethalin	104 ± 33	94 ± 30	100 ± 32	106 ± 34	95 ± 30	117 ± 37	115 ± 36

Table S5. Specific fluxes during the seasonal campaigns (mg day⁻¹ km⁻²).

		Ternoise	Planquette	Créquoise	Bras de Brône	Course	Dordogne	Huitrepin	Canche 0	Canche 1	Canche 2	Canche 3	Canche 4	Canche 5	Canche 6	Canche 7
February 16	atrazine	61	32	93	72	122	241	95	32	41	37	34	43	54	52	51
	diflufenican	16	8	7	13	14	124	19	10	12	11	11	10	9	13	14
	ethofumesathe	<1	<1	<1	<1	<1	33	9	<1	<1	<1	<1	<1	<1	2	2
	metolachlor	7	11	9	7	14	19	9	4	4	5	5	5	6	8	7
	pendimethalin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
May 16	atrazine	59	32	96	70	95	175	73	35	48	44	44	38	33	37	38
	diflufenican	10	5	11	8	17	75	14	8	9	7	9	9	9	10	10
	ethofumesathe	113	19	269	38	111	24	24	25	40	39	48	37	28	34	41
	metolachlor	21	14	2554	12	12	19	156	9	18	20	138	111	75	68	52
	pendimethalin	<1	<1	<1	<1	<1	12	2	15	6	7	7	7	7	3	4
July 16	atrazine	47	25	71	52	60	109	49	25	37	29	31	32	32	33	36
	diflufenican	<1	1	<1	3	2	13	5	3	2	2	2	2	2	2	2
	ethofumesathe	2	<1	<1	<1	<1	5	2	2	<1	<1	1	2	2	1	2
	metolachlor	25	4	11	16	6	10	6	7	9	8	6	11	9	5	4
	pendimethalin	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
November 16	atrazine	38	15	44	22	40	51	26	20	26	23	19	16	22	26	28
	diflufenican	10	58	27	50	11	302	61	19	11	15	10	11	9	14	21
	ethofumesathe	<1	<1	<1	8	<1	33	5	<1	<1	<1	<1	<1	<1	<1	<1
	metolachlor	<1	4	<1	6	4	24	10	4	<1	<1	<1	<1	2	2	12
	pendimethalin	12	8	121	66	53	586	66	7	8	8	13	14	20	28	26

Table S6. Dissolved concentrations of pesticides at *Canche* 5 sampling site (ng L⁻¹).

	atrazine	diflufenican	ethofumesat	metolachlor	pendimethalin
10-feb.-16	14	7	1	10	<1
16-feb.-16	-	4	1	5	<1
22-feb.-16	12	1	<1	1	<1
2-march-16	8	3	<1	2	<1
8-march-16	10	2	<1	1	<1
22-march-16	10	1	<1	2	1
5-april-16	12	4	<1	6	<1
19-april-16	12	2	<1	1	<1
27-april-16	9	4	7	3	<1
3-may-16	10	3	8	4	1
18-may-16	10	2	61	21	4
31-may-16	15	9	61	148	6
13-june-16	16	13	15	46	2
18-july-16	12	1	1	3	<1
9-aug.-16	11	1	<1	1	<1
24-aug.-16	14	1	<1	1	<1
9-sept.-16	12	2	<1	3	<1
14-sept.-16	12	1	<1	1	<1
15-sept.-16	10	1	<1	1	<1
16-sept.-16	13	1	<1	1	<1
17-sept.-16	12	3	1	7	1
18-sept.-16	14	3	3	5	1
19-sept.-16	0	1	1	4	1
22-sept.-16	9	1	<1	1	1
28-sept.-16	9	<1	<1	<1	1
11-oct.-16	11	1	<1	1	2
20-oct.-16	11	2	<1	1	3
25-oct.-16	9	1	<1	1	2
27-oct.-16	15	3	<1	2	4
29-oct.-16	11	3	<1	3	2
31-oct.-16	11	1	1	2	1
3-nov.-16	10	1	<1	<1	2
9-nov.-16	11	5	<1	1	8
14-nov.-16	12	5	<1	1	10
23-nov.-16	11	5	1	1	6
15-dec.-16	13	4	1	1	3
5-jan.-17	13	1	<1	<1	3
11-jan.-17	15	2	<1	1	4
26-jan.-17	15	2	<1	<1	1
8-feb.-17	9	2	1	1	2

Table S7. Average dissolved concentrations of pesticides at *Canche 5* sampling site (passive samplers; ng L⁻¹).

		atrazine	ethofumesat	diflufenican	metolachlor	pendimethalin
2-april-16	19-avr.-16	9	35	2	9	2
19-april-16	3-may-16	8	48	2	11	2
3-may-16	18-may-16	8	40	2	32	2
18-may-16	31-may-16	10	127	12	71	30
31-may-16	13-june-16	11	9	3	25	1
13-june-16	19-july.-16	9	83	5	128	7
19-july-16	2-aug-16	9	47	3	52	4
2-aug.-16	9-aug-16	11	2	2	5	1
9-aug.-16	24-aug-16	9	1	1	1	1
24-aug.-16	9-sept.-16	8	1	1	2	1
9-sept.-16	22-sept.-16	8	2	1	2	<1
22-sept.-16	28-sept.-16	8	2	1	1	<1
28-sept.-16	11-oct.-16	8	<1	1	2	1
11-oct.-16	27-oct.-16	12	1	3	3	4
27-oct.-16	9-nov.-16	11	<1	3	1	9
9-nov.-16	23-nov.-16	11	1	10	2	17
23-nov.-16	7-dec.-16	10	<1	3	2	3
7-dec.-16	22-dec.-16	8	<1	2	1	1
22-dec.-16	11-jan.-17	13	<1	3	1	3
5-jan.-17	11-jan.-17	21	<1	4	1	4
11-jan.-17	26-jan.-17	11	<1	6	1	4
26-jan.-17	8-feb.-17	9	<1	3	1	2
8-feb.-17	22-feb.-17	11	1	2	<1	<1
22-feb.-17	10-mar-17	9	<1	5	4	1
6-mar-17	22-mar-17	10	3	4	8	<1

Table S8. Dissolved concentrations of pesticides in ground water during summer and winter (ng L⁻¹).

[illegible]

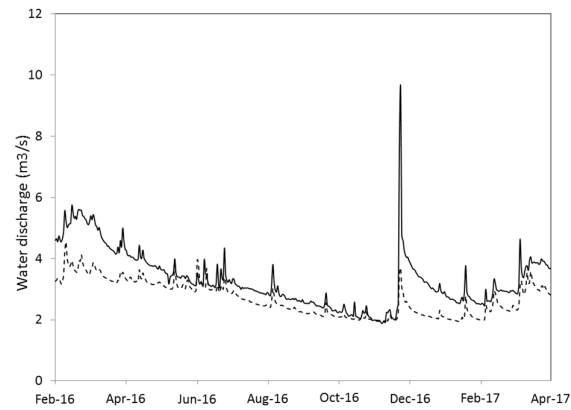


Figure S1. Comparison between the measured water discharge at the *Course* gauging station and the estimation method using as reference the gauging station on the main stream. The dotted line refers to the estimation method and the full line refers to the measured values. For the cross validation, high-frequency data were compared to the flow discharge calculated with the cited method at Attin (for further details see [17]).

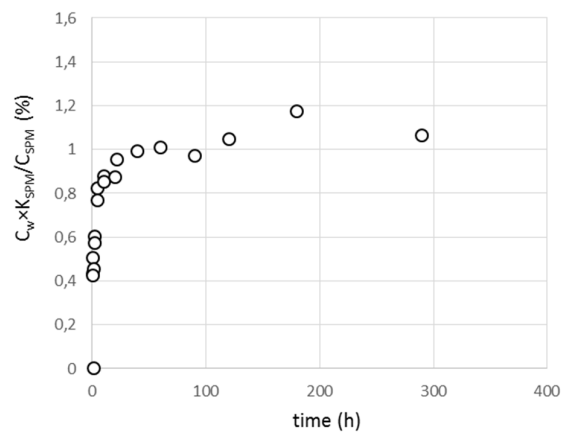


Figure S2. Transport kinetics of diflufenican from the SPM-sorbed state to the dissolved phase. Dissolved concentration is expressed relatively to the concentration at equilibrium ($C_w \times K_{SPM} / C_{SPM}$).

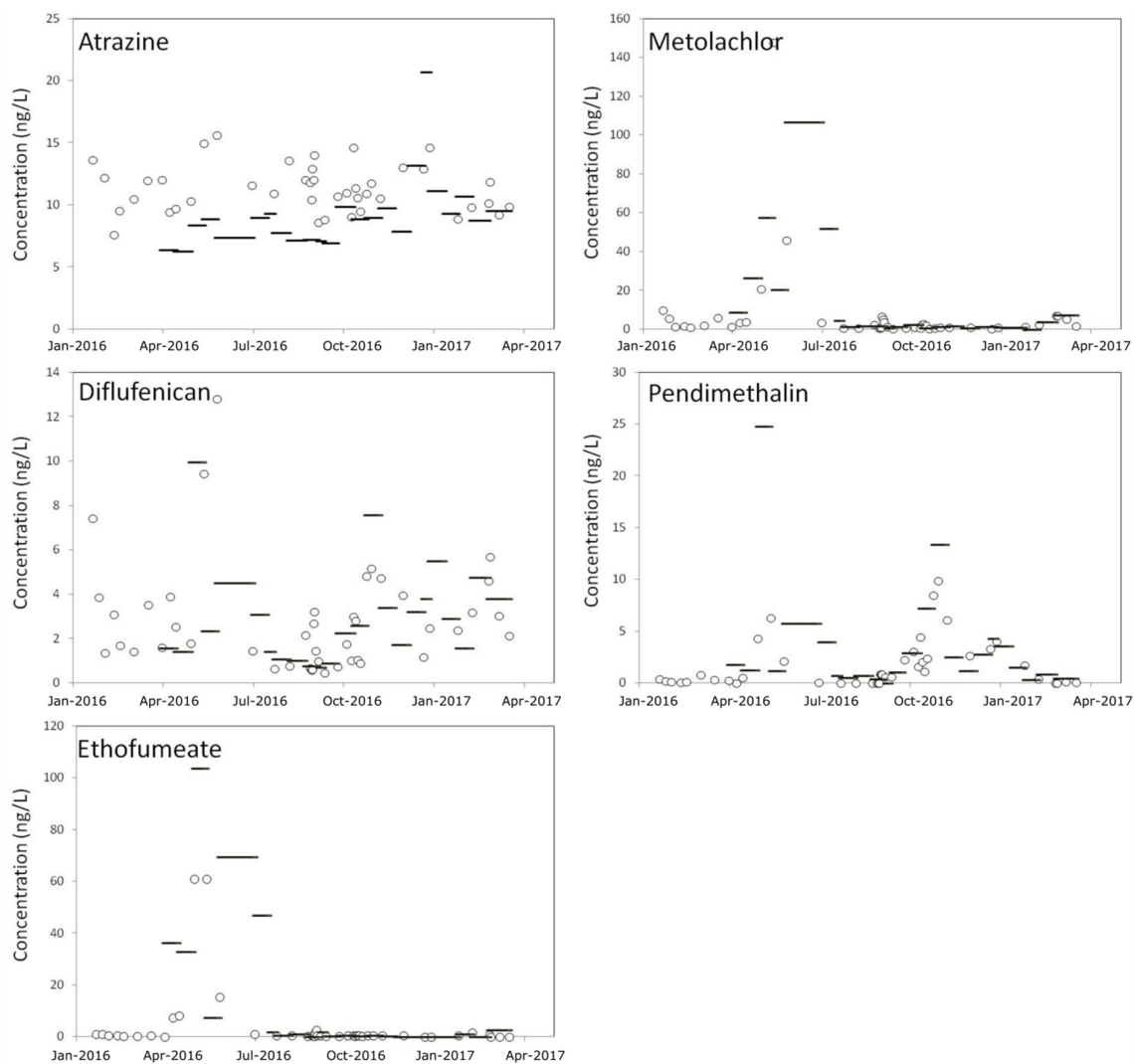


Figure S3. Dissolved concentration measured at *Canche 5* sampling site. Lines refer to the passive samplers-derived contamination level and circles refer to the contamination level monitored by grab sampling.

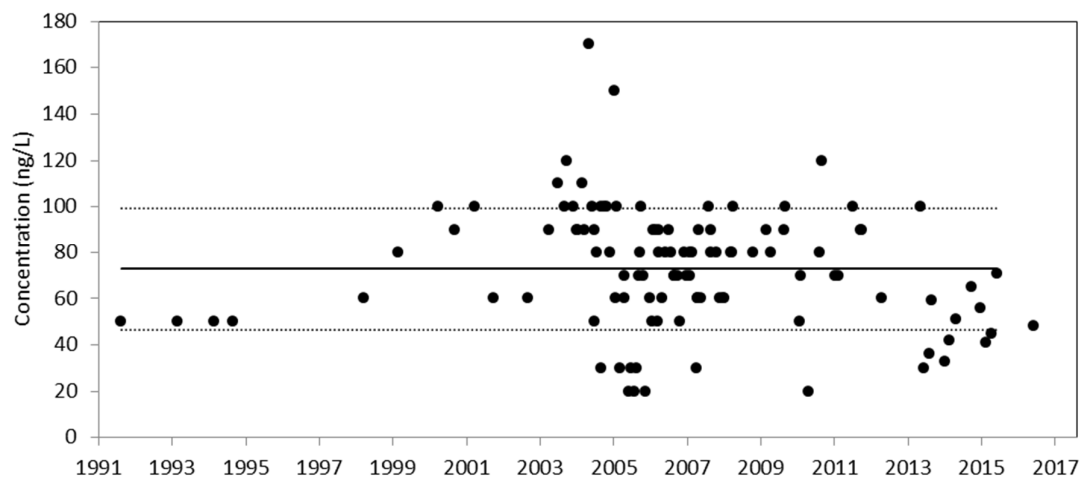


Figure S4. Dissolved concentration of atrazine at pz7 sampling point (groundwater). Circle symbols refer to the results obtained by measurements conducted and provided by the Water Agency Artois-Picardie between 1991 and 2016. The solid and dashed lines represent the mean value and the 95% confidence interval respectively.