Supporting information to

Continuous high-frequency pesticide monitoring to observe the unexpected and the

overlooked

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Section S1

Analytics of MS²Field

Table S1: Analytics by MS²Field. Compounds in bold were quantified with an isotope labeled internal standard (ISTD) that had the nearest retention time. The limit of detection was not determined. The workflow of MS²Field does not allow for the proper estimation of a measurement error (i.e., measuring multiple times the same sample). Relative recovery not calculated for compounds found below LOQ. Compounds not quantifiable due to poor calibration curves.

Name	Class	In samples	LOQ (ng/l)	Relative Recovery (%)	ISTD
Acetamiprid	Insecticide	Found	10	48	Metamitron D5
Atrazine	Herbicide	Found below LOQ	8		Atrazin D6
Atrazine-desethyl-desisopropyl	Metabolite	Found	15	90	Atrazine-Desethyl 15N3
Azoxystrobin	Fungicide	Found	5	139	Azoxystrobin D4
Azoxystrobin free acid	Metabolite	Found	20	87	Azoxystrobin D4
Bentazon	Herbicide	Not found	20		*Bentazon D6*
Benzotriazol	Corrosion inhibitor	Found below LOQ	80		Benzotriazol D4
Boscalid	Fungicide	Not found	10		*Boscalid D4*
Bupirimate	Fungicide	Not found	5		*Metamitron D5*
Chloridazon	Herbicide	Found below LOQ	15		Chloridazon D5
Chlortoluron	Herbicide	Not found	20		Pyrimethanil D5
Clothianidin	Insecticide	Found	15	76	Clothianidin D3
Cyproconazol	Fungicide	Found below LOQ	35		Epoxiconazol D4
Cyprodinil	Fungicide	Found	10	61	Cyprodinil D5
Diazinon	Insecticide	Not found	10		Diazinon D10
Difenoconazole	Fungicide	Found	65	91	Metconazol D6
Dimethenamide	Herbicide	Found	15	67	Dimethenamid D5
Dimethoate	Insecticide	Found	15	70	Chloridazon D5
Diuron	Herbicide	Found	6	79	Diuron D6
Epoxiconazole	Fungicide	Found	15	76	Epoxiconazol D4
Ethofumesat	Herbicide	Not found	40		Isoproturon D6
Fenhexamid	Herbicide	Found	4	74	Fenhexamid D3
Fenpyrazimin	Fungicide	Found	15	66	Myclobutanil D4
Fluopyram	Herbicide	Found	4	84	Fluopyram D4
Flusilazol	Fungicide	Not found	40		Epoxiconazol D4
Haloxyfop	Herbicide	Not found	20		Haloxyfop D4
Imidacloprid	Insecticide, caustic	Not found	20		Imidacloprid D4

Iprodione	Fungicide	Not quantifiable	6		Boscalid D4
Iprovalicarb	Fungicide	Not found	10		Epoxiconazol D4
Isoproturon	Herbicide	Not found	10		Isoproturon D6
Kresoxim-methyl	Fungicide	Found below LOQ	35		Epoxiconazole D4
Lenacil	Herbicide	Not found	20		Diuron D6
Mecoprop	Herbicide	Found	4	78	Mecoprop D6
Metalaxyl	Fungicide	Not quantifiable	50		Metalaxyl D6
Metamitron	Herbicide	Found	5	85	Metamitron D5
Methoxyfenozide	Insecticide	Found	15	68	Dimethenamid D5
Metolachlor	Herbicide	Found	4	73	Metolachlor D6
Metribuzin	Herbicide	Found	70	77	Metribuzin D3
Monuron	Herbicide	Not found	10		Thiacloprid D4
Myclobutanil	Fungicide	Found	3	81	Myclobutanil D4
Napropamide	Herbicide	Found	7	77	Fluopyram D4
Neotam	Sweetener	Not found	15		Metalaxyl D6
Nicosulfuron	Herbicide	Found	30	112	Simazin D5
DEET	Insect repellent	Found	8	77	N-N-diethyl-3-methylbenzamid (DEET) D10
Oxadixyl	Fungicide	Found	6	107	Thiacloprid D4
Penconazole	Fungicide	Found	15	80	Diazinon D10
Pirimicarb	Insecticide	Not quantifiable	2		Thiacloprid D4
Propamocarb	Fungicide	Not found	20		Propamocarb free base D6
Propiconazole	Fungicide	Found	6	74	Diazinon D10
Propyzamide	Herbicide	Not found	2		Propyzamide D3
Pyrimethanil	Fungicide	Found	4	74	Pyrimethanil D5
Simazine	Herbicide	Found	2	104	Simazin D5
Simeton	Herbicide	Not quantifiable	4		Imidacloprid D4
Tebuconazole	Fungicide	Found	6	75	Tebuconazole D9
Tebufenozide	Insecticide	Found below LOQ	30		Tebuconazole D9
Terbutylazine	Herbicide	Found	2	76	Terbutylazine D5
Terbutylazin-desethyl	Herbicide	Found	3	69	Atrazin D5
Thiacloprid	Insecticide	Found	8	68	Thiacloprid D4
Thiamethoxam	Insecticide	Found below LOQ	100		Clothianidin D3
Trifloxystrobin	Fungicide	Not quantifiable	100		Metconazol D6

Section S2

Analytics by Interkantonales Labor, Schaffhausen

Samples were analyzed using direct injection liquid chromatography coupled to mass spectrometry (*Table S2*). The target list included 93 compounds and metabolites (Table S3). Samples were centrifuged and a solution containing isotope-labeled internal standards (ISTD) was spiked. Randomly selected samples were spiked with a standard solution in order to assess relative recovery of the compounds. An injection volume of 120 μL was used and chromatographic separation was performed (Agilent Zorbax Eclipse XDB C18, 2.1 x 100 mm, 1.8 μm), applying a water-methanol gradient (both containing 0.1% formic acid/formate buffer). The measurements were performed on a triple quadrupole mass spectrometer (Agilent TripleQuad 6490A) after electrospray ionization acquiring at least to MRM transitions (quantifier and qualifier) per compound. Quantification of the target compounds was performed using the Masshunter Software (Agilent). LOQ values were in the range of 7 – 40 ng/l with an uncertainty ranging between 10% – 35% (Table S3).

Table S2: Details of the method used by Interkantonales Labor, Schaffhausen.

Internal Method Number	M-0473	M-0462	M-0488
Internal Method Version	1	3	1
Sample preparation	centrifuge	centrifuge	centrifuge
Sample enrichment	no	no	no
Injection volume/ μl	120	120	120
LC System	Agilent Infinity 1290	Agilent Infinity 1290	Agilent Infinity 1290
MS System	Agilent TripleQuad 6490A	Agilent TripleQuad 6490A	Agilent TripleQuad 6490A

Quantification Software	Agilent Masshunter	Agilent Masshunter	Agilent Masshunter
LC column	Agilent Zorbax Eclipse XDB C18, 2.1 x 100 mm, 1.8µm	Agilent Zorbax SB-Aq, 2.1 x 100 mm, 1.8 µm	Waters Acquity UPLC BEH C18, 130 Å, 2.1 × 75 mm, 1.7 µm
Eluent A	water + 0.1% formic acid /formate buffer	water + 0.5% formic acid	water + 0.1% formic acid /formate buffer
Eluent B	methanol + 0.1% formic acid /formate buffer	methanol + 0.5% formic acid	methanol + 0.1% formic acid /formate buffer
Isotop-labeled internal standard used	yes	yes	yes
Independent reference material used	yes	yes	yes
Relative recovery checked	yes	yes	yes

Table S3: Analytics by Interkantonales Labor, Schaffhausen. We are not for which compound the corresponding isotope labeled standards was used for quantification.

Internal Method Number	Parameter	Limit of quantification (µg/l)	Uncertainty (%)
M-0473	1H-Benzotriazol	0.04	10%
	4-/5-Methylbenzotriazol	0.015	10%
	Atenolol	0.012	10%
	Atrazin	0.035	15%
	Azithromycin	0.034	25%
	Azoxystrobin	0.025	15%
	Bezafibrat	0.016	25%
	Boscalid	0.033	20%
	Carbamazepin	0.033	10%
	Carbendazim	0.017	10%
	Chloridazon	0.007	10%
	Chloridazon-desphenyl	0.015	10%
	Chlorpyrifos	0.027	15%
	Chlortoluron	0.011	10%
	Clarithromycin	0.03	20%
	Cyproconazol	0.018	15%
	Cyprodinil	0.026	25%
	DEET (Diethyltoluamid)	0.016	30%

	Diazinon	0.013	10%
	Diclofenac	0.02	15%
	Dimethoat	0.012	10%
	Diuron	0.015	15%
	Epoxiconazol	0.016	15%
	Erythromycin	0.02	30%
	Erythromycin-H2O	0.015	25%
	Ethofumesat	0.033	20%
	Imidacloprid	0.014	10%
	Iprovalicarb	0.024	15%
	Isoproturon	0.025	15%
	Linuron	0.007	10%
	Mefenaminsäure	0.015	10%
	Metalaxyl	0.015	15%
	Metamitron	0.019	10%
	Metazachlor	0.009	15%
	Metformin	0.034	20%
	Methoxyfenozid	0.011	15%
	Metolachlor	0.017	15%
	Metoprolol	0.009	10%
	Metribuzin	0.015	10%
	Napropamid	0.016	15%
	Naproxen	0.029	25%
	Nicosulfuron	0.011	35%
	Pirimicarb	0.014	10%
	Propamocarb	0.022	10%
	Pyrimethanil	0.02	20%
	Sotalol	0.017	10%
	Sulfamethazin	0.013	10%
	Sulfamethoxazol	0.01	15%
	Tebuconazol	0.014	10%
	Terbuthylazin	0.014	20%
	Terbutryn	0.009	10%
	Thiacloprid	0.009	10%
	Thiamethoxam	0.008	10%
	Trimethoprim	0.028	15%
M-0462	2,4-D	0.02	30%
	Acesulfam-K	0.04	30%
	Azoxystrobinsäure	0.02	30%
	Bentazon	0.02	30%
	Chlorothalonil Metabolit R417888	0.02	30%
	Dichlorprop	0.04	30%
	Dimethenamid-ESA	0.02	30%
	Dinoseb	0.02	30%
	MCPA	0.02	30%
	Mecoprop	0.02	30%
	Mesotrion	0.02	30%

	Metazachlor ESA	0.04	30%
	Metolachlor-ESA	0.04	20%
	Metolachlor-OXA	0.04	20%
	Propachlor-ESA	0.02	20%
	Propachlor-OXA	0.04	20%
	Sulcotrion	0.04	30%
M-0488	Acetamiprid	0.022	25%
	Bupirimat	0.025	25%
	Chlorantraniliprol	0.022	20%
	Clothianidin	0.029	25%
	Diflufenican	0.016	20%
	Dimethachlor	0.017	20%
	Dimethenamid	0.017	25%
	Fenhexamid	0.02	20%
	Fenoxycarb	0.026	25%
	Fenpyrazamin	0.021	30%
	Fludioxonil	0.04	30%
	Flufenacet	0.019	25%
	Fluopyram	0.014	25%
	Foramsulfuron	0.019	35%
	Haloxyfop	0.024	25%
	Mesosulfuron-methyl	0.03	25%
	Methiocarb	0.031	30%
	Methomyl	0.027	25%
	Propiconazol	0.017	20%
	Propyzamid	0.009	20%
	Spiroxamin	0.018	30%
	Tebufenozid	0.02	25%

Section S3

Analytics by InterLabor, Belp

The water sample is filtered through a paper filter and the pH adjusted to 7. With each series, a blank sample (tap water) and a recovery sample (spiked tap water at 0.1 µg/l) is prepared and analysed. An aliquot of 250 ml of each sample is used for further sample preparation. A solution of several isotope-labeled internal standards (ISTD) is added to each sample.

- Sample preparation for determination of pesticides (higher polarity / higher masses) by LC-MS/MS

For solid phase extraction (SPE) (Oasis HLB 3 CC, 60 mg), the cartridges are conditioned with 3 ml of methanol and 3 ml of pure water prior to slowly pass the 250 ml aliquote of each sample. The cartridges are brought to dryness with suction and subsequently eluated with 3 ml of methanol. The collected eluate in a PE-tube is evaporated to dryness (TurboVap, 45 °C). The residues are brought back into solution with 500 µl of acetonitrile. Extract is transferred to a vial for HPLC injection. Standard solutions of 200 ng/ml and 20 ng/ml in acetonitrile are prepared for external calibration of the system.

- Sample preparation for determination of pesticides (lower polarity / lower masses) by GC-MS/MS

The 250 mL aliquote is extracted with a first quantity of 8 ml dichloromethane (DCM) in a separating funnel. The DCM is collected and the extraction is repeated with a second quantity of 8 ml of DCM. The DCM of both extraction steps are combined and dried with little sodium sulfate. In a PE-tube, the DCM is evaporated to dryness (TurboVap, 45 °C). The residues are brought back into solution with 5 ml of 0.05 % (v/v) formic acid in acetonitrile. 100 µl are transferred to a vial for GC analysis (higher concentrated analytes). The remaining solution

again evaporated to dryness (TurboVap, 45 °C). The residues are brought back into solution with 500 µl of 0.05 % (v/v) formic acid in acetonitrile and transferred to second vial for GC analysis (lower concentrated analytes). Standard solutions of 200 ng/ml and 20 ng/ml in acetonitrile are prepared for external calibration of the system.

- Analysis of water samples

The prepared solutions are analysed by liquid chromatography with tandem mass spectrometry (LC-ESI-MS/MS) and gas chromatography with tandem mass spectrometry (GC-EI-MS/MS). Each positive signal is verified by the signal ratio of two or more mass fragments. This allows obtaining results with a high specificity. In addition, the preparation and analysis of a spiked water sample and the usage of internal standards are helpful to control the accuracy of the results. In combination of both techniques some 500 compounds are covered.

- System and components

HPLC: Agilent Technologies, HPLC 1290 Infinity

MS/MS: Sciex, API 6500+

ESI source: Sciex, Ion Drive Turbo V Ion Source with TurboIonSpray

HPLC column: Phenomenex Aqua, 75 x 2.0 mm, 3 µm, 125 Å (00C-4311-B0)

GC-MS/MS: Agilent Technologies, GC-MS Triple Quad 7000C

GC column: Zebron ZB-Multiresidue-1, 30 m x 0.25 mm, 0.25 µm (7HG-G016-11)

- Limit of quantification

The analytical method is capable of quantifying most of the analytes at a lower limit of 0.01 µg/l (related to the water sample) . Significant detected signals with concentrations below

0.01 µg/l will be reported as "trace". Some analytes may have a higher limit of quantification due to sensitivity, interferences or partial loss during sample preparation.

In this study, we were not provided with a list of compounds with corresponding LOQ values. Still, we are interested in compounds that were measured at high concentrations.

Section S4

Estimation of the measurement error for *MS²Field*

The estimatation of the *MS²Field* measurement errors per compound exploits the high sampling frequency in dry periods. In fact, we expect that concentration levels may change slowly due to the lack of meteorological drivers, and therefore, differences in concentrations measured in samples collected 20 minutes apart should reflect the measurement error. For this analysis, we select six successive data points collected in each evening of June 28th, June 29th and 30th (evening was the period with lower fluctuations of the concentrations as shown in detail in the companion manuscript revealing the presence of diel fluctuations).

As shown in the table below, we calculate one mean concentration using C1, C3 and C5 and another mean concentration using C2, C4 and C6 (three replicas averaging possible trends in concentrations during the two hours. Then, we calculate the absolute median relative % difference. The calculation is repeated using the concentrations measured on June 29th and June 30th. Finally, we calculate a mean absolute median relative % difference using the three values for the three days and we keep the maximum value as the final measurement error. This approach is used for compounds with concentrations above the LOQ at all selected times.

Date and time	Concentration	Mean concentration	Absolute median relative % difference
6.28.2019 19:07:53	C1	M1=(C1+C3+C5)/3	|M2-M1|/((M2+M1)/2) * 100
6.28.2019 19:28:00	C2		
6.28.2019 19:48:08	C3		
6.28.2019 20:08:15	C4	M2=(C2+C4+C6)/3	
6.28.2019 20:28:23	C5		
6.28.2019 20:48:31	C6		

For compounds with concentrations below the corresponding LOQ in at least one selected time, we calculate a measurement error using samples that were spiked with known

concentrations of the target compounds during the quality check routine of MS2Field, as shown in the table below. On June 28th, 29th and 30th there were three spikes, one per day. To the spiked concentrations, we substracted the concentration measured at the previous time step (because the concentrations are below the LOQ, we substracted a concentration equal to half the LOQ). Then, we calculate an absolute median relative % difference using each combination without repetition of the calculated differences between two days (i.e., 28th-29th, 28th-30th, 29th-30th). Finally, we keep the maximum absolute median relative % difference among the three values for the three combinations.

Date and time	Concentration before spike	Concentration after spike	Difference	median relative % difference
2.28.2019	C0_A	C1_A	C_A=C1_A-C0_A	$|C\_B-C\_A|/((C\_B+C\_A)/2)$
2.29.2019	C0_B	C1_B	C_B=C1_B-C0_B	* 100

Table S4: Estimated measurement error for MS^{2}Field

Name	Abbreviation	Error
Acetamiprid	Acetamiprid	8
Azoxystrobin	Azoxystrobin	7
Azoxystrobin_free_acid	Azoxystrobin-TP	4
Clothianidin	Clothianidin	4
Cyprodinil	Cyprodinil	11
DEET	DEET	6
Dimethenamide	Dimethenamide	3
Diuron	Diuron	7
Epoxiconazole	Epoxiconazole	5
Fenhexamid	Fenhexamid	7
Fenpyrazamin	Fenpyrazamin	5
Fluopyram	Fluopyram	3
Mecoprop	Mecoprop	3
Metamitron	Metamitron	10
Metolachlor	Metolachlor	1
Myclobutanil	Myclobutanil	7
Nicosulfuron	Nicosulfuron	5
Napropamide	Napropamide	5
Oxadixyl	Oxadixyl	4
Pyrimethanil	Pyrimethanil	3
Simazin	Simazin	5

Tebuconazole	Tebuconazole	6
Terbutylazine	Terbutylazine	9
Terbutylazin_desethyl	Terbutylazin-TP	6
Thiacloprid	Thiacloprid	9

Section S5

Hydrological classification

Table S5: Summary of the large rain events.

Date start	Date end	Sum rain over event (mm)	Maximum intensity in the event (mm/10 min)	Average intensity in the event (mm/10 min)	Duration of the event (hours)	Minimum water level in the event (m)	Maximum water level in the event (m)	Standard deviation of the water level in the event (m)
28.05.2019 02:20	28.05.2019 06:30	3.2	1.2	0.1	4.2	0.158	0.264	0.015
10.06.2019 06:00	10.06.2019 07:30	1.9	1.1	0.2	1.5	0.121	0.247	0.015
10.06.2019 10:10	10.06.2019 13:30	18.2	10.4	0.9	3.3	0.121	0.315	0.022
10.06.2019 20:00	11.06.2019 03:10	16.4	1.7	0.4	7.2	0.121	0.315	0.022
12.06.2019 01:00	12.06.2019 07:20	22.1	1.4	0.6	6.3	0.121	0.449	0.042
15.06.2019 19:00	16.06.2019 01:00	8.3	3.8	0.2	6.0	0.149	0.449	0.052
01.07.2019 22:20	02.07.2019 00:50	27.2	14.2	1.7	2.5	0.121	0.463	0.023
07.07.2019 03:00	07.07.2019 05:50	6.1	1.2	0.3	2.8	0.121	0.463	0.022

Table S6. Summary of the small rain events.

Date start	Date end	Sum rain over event (mm)	Maximum intensity in the event (mm/10 min)	Average intensity in the event (mm/10 min)	Duration of the event (hours)	Minimum water level in the event (m)	Maximum water level in the event (m)	Standard deviation of the water level in the event (m)
27.05.2019 21:30	27.05.2019 21:30	0.2	0.2	0.2	0.0	0.173	0.176	0.001
28.05.2019 09:40	28.05.2019 10:30	0.3	0.1	0.1	0.8	0.170	0.178	0.002
28.05.2019 21:00	28.05.2019 22:40	2.1	0.5	0.2	1.7	0.163	0.212	0.017
29.05.2019 12:30	29.05.2019 13:10	0.9	0.4	0.2	0.7	0.155	0.205	0.015
29.05.2019 15:20	29.05.2019 15:20	0.2	0.2	0.2	0.0	0.159	0.177	0.004
10.06.2019 17:40	10.06.2019 17:40	0.1	0.1	0.1	0.0	0.149	0.168	0.005
15.06.2019 00:00	15.06.2019 00:20	0.3	0.2	0.1	0.3	0.165	0.170	0.001
16.06.2019 07:40	16.06.2019 07:50	0.2	0.1	0.1	0.2	0.153	0.157	0.001
18.06.2019 18:40	18.06.2019 18:40	0.2	0.2	0.2	0.0	0.147	0.150	0.001
19.06.2019 05:00	19.06.2019 05:00	0.1	0.1	0.1	0.0	0.143	0.147	0.001
19.06.2019 20:40	19.06.2019 20:50	0.7	0.5	0.4	0.2	0.145	0.157	0.004
20.06.2019 04:30	20.06.2019 04:30	0.1	0.1	0.1	0.0	0.142	0.164	0.006
20.06.2019 10:50	20.06.2019 12:40	1.2	0.2	0.1	1.8	0.140	0.155	0.004
20.06.2019 17:20	20.06.2019 17:40	1	0.8	0.3	0.3	0.146	0.169	0.006
21.06.2019 23:00	22.06.2019 01:10	1.6	0.3	0.1	2.2	0.142	0.173	0.008

Section S6

Concentrations measured with *MS²Field* and comparison with NAWA-Trend
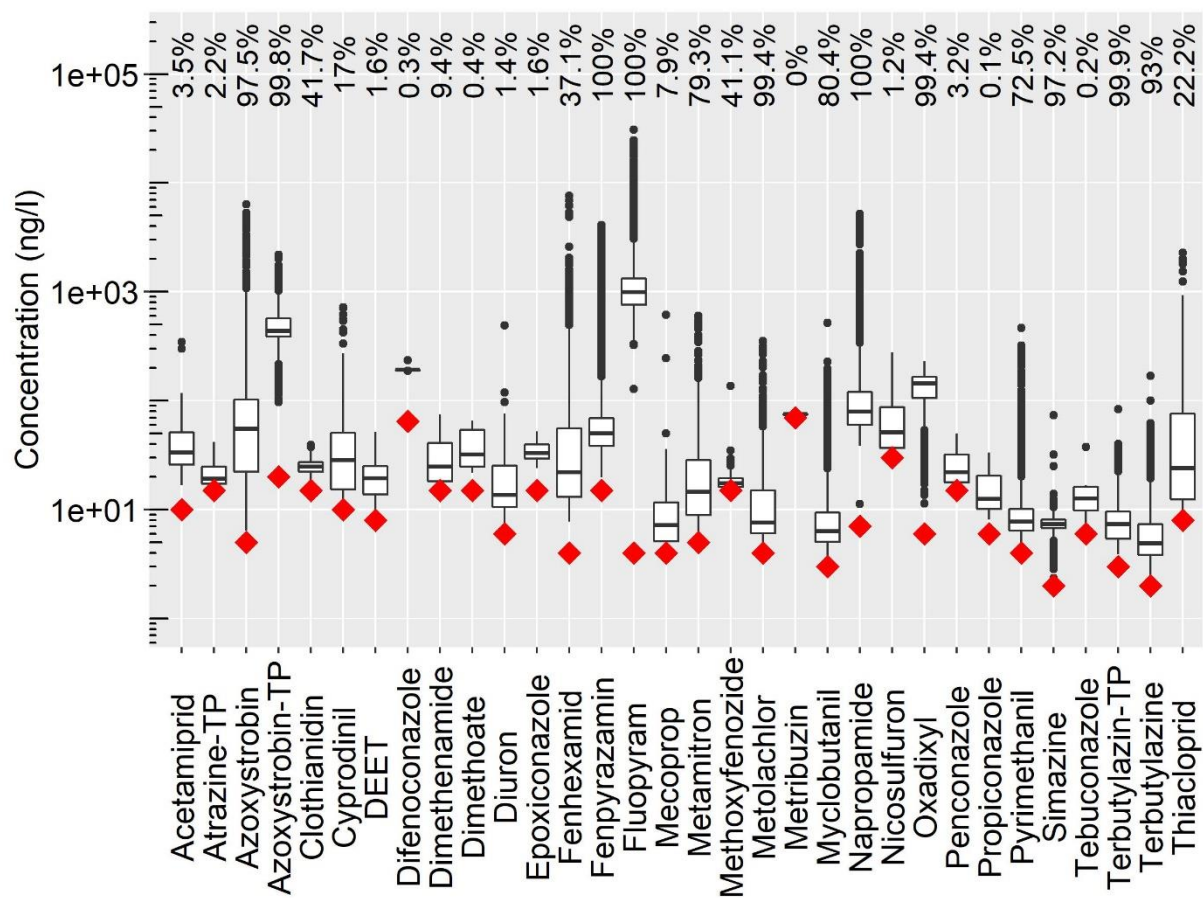
Figure S1: Concentrations measured with MS²Field represented in log10 scale, with values smaller than the corresponding LOQ not shown. LOQ values shown as red diamonds. The percentage of concentration values above LOQ, excluding data gaps, per compound over the monitoring is reported above the boxplots. Azoxystrobin-TP corresponds to azoxystrobin free acid and Terbutylazin-TP corrsponds to terbutylazin desethyl.
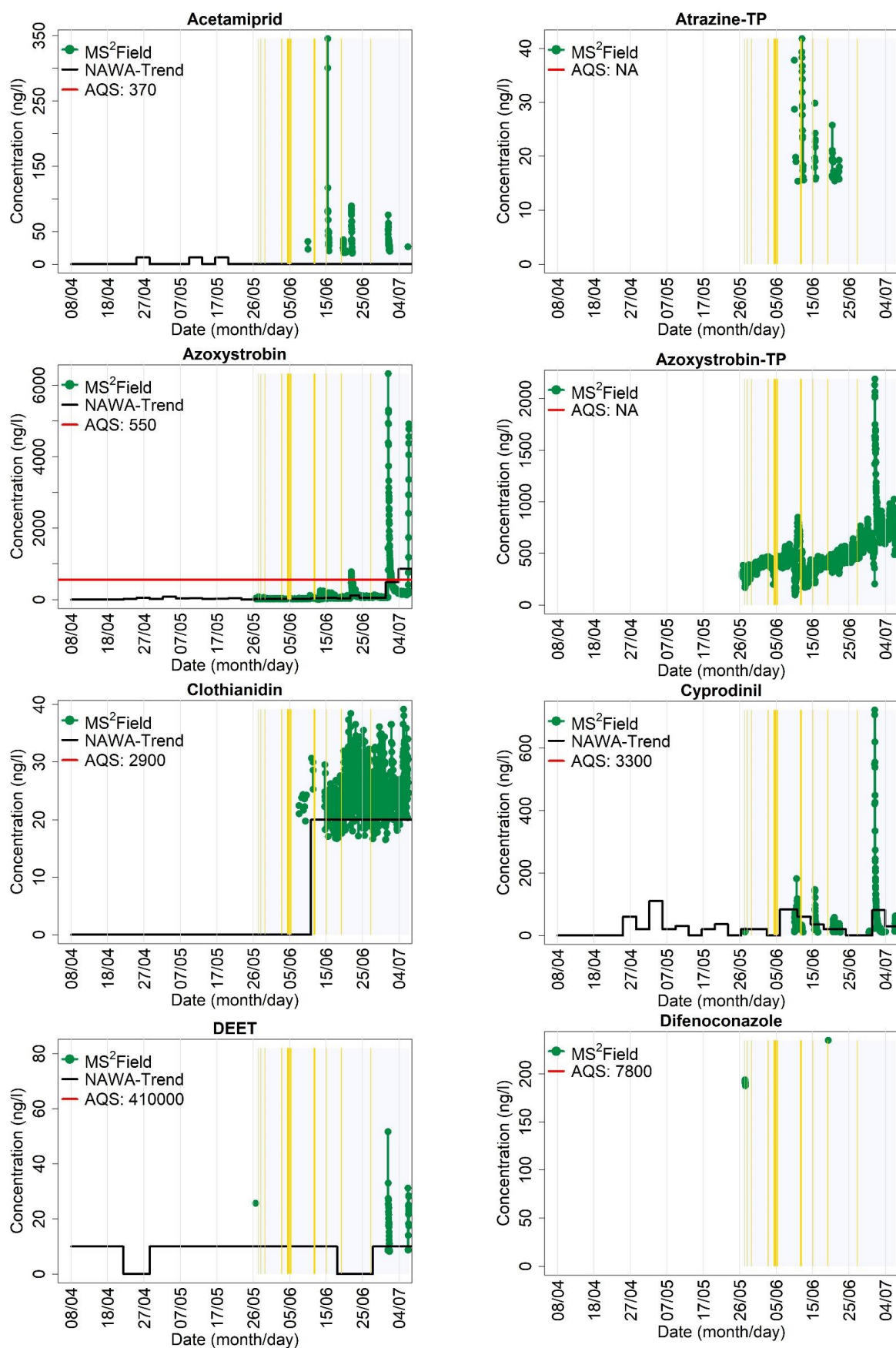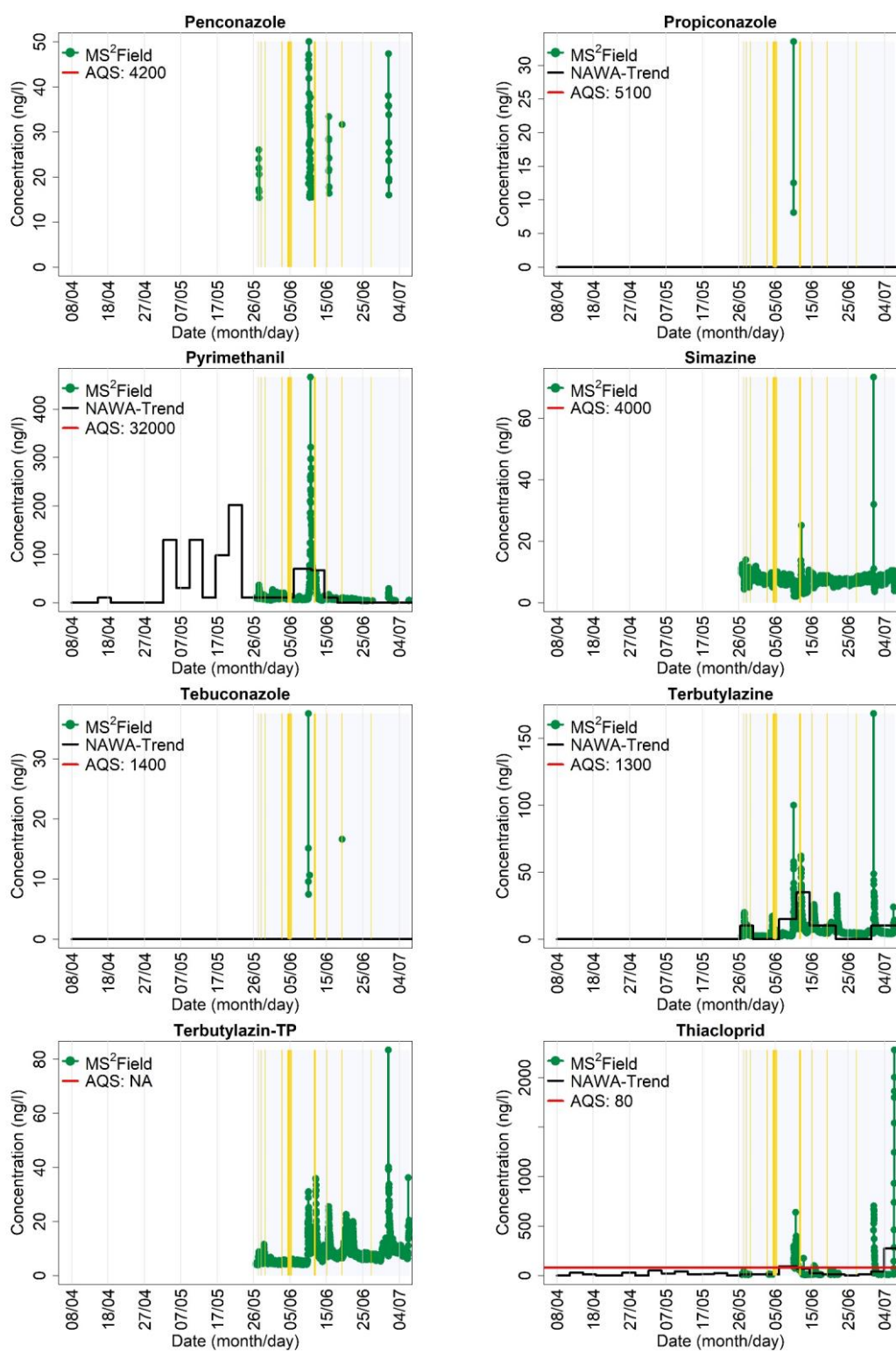
Figure S2: Concentration time series of compounds measured by MS²Field with concentrations above

LOQ (green line and bullets). In black, the time series of the compounds that were also measured by

NAWA-Trend. MS^{2}Field was used from May 27th to July 7th (light grey background) and NAWA-Trend collected 3.5 days composite samples from April to July. In red, the acute quality standard (AQS). Vertical bars in gold show periods with data gaps due to maintenance of MS^{2}Field. Atrazine-TP corresponds to atrazine desethyl desisopropyl and Azoxystrobin-TP corresponds to azoxystrobin free acid.
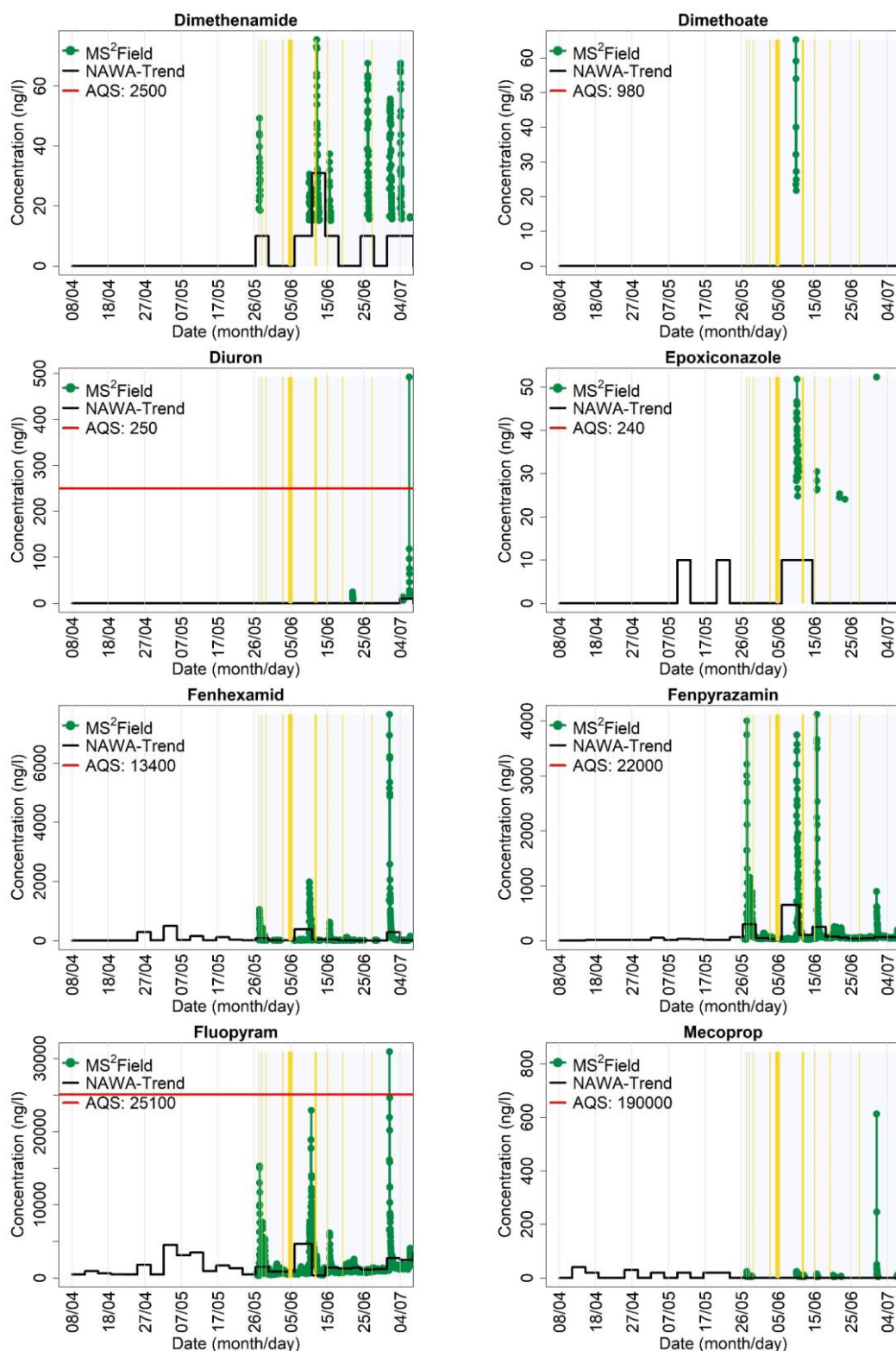
Figure S3: Concentration time series of compounds measured by MS²Field with concentrations above LOQ (green line and bullets). In black, the time series of the compounds that were also measured by NAWA-Trend. MS²Field was used from May 27th to July 7th (light grey background) and NAWA-Trend collected 3.5 days composite samples from April to July. In red, the acute quality standard (AQS). Vertical bars in gold show periods with data gaps due to maintenance of MS²Field.
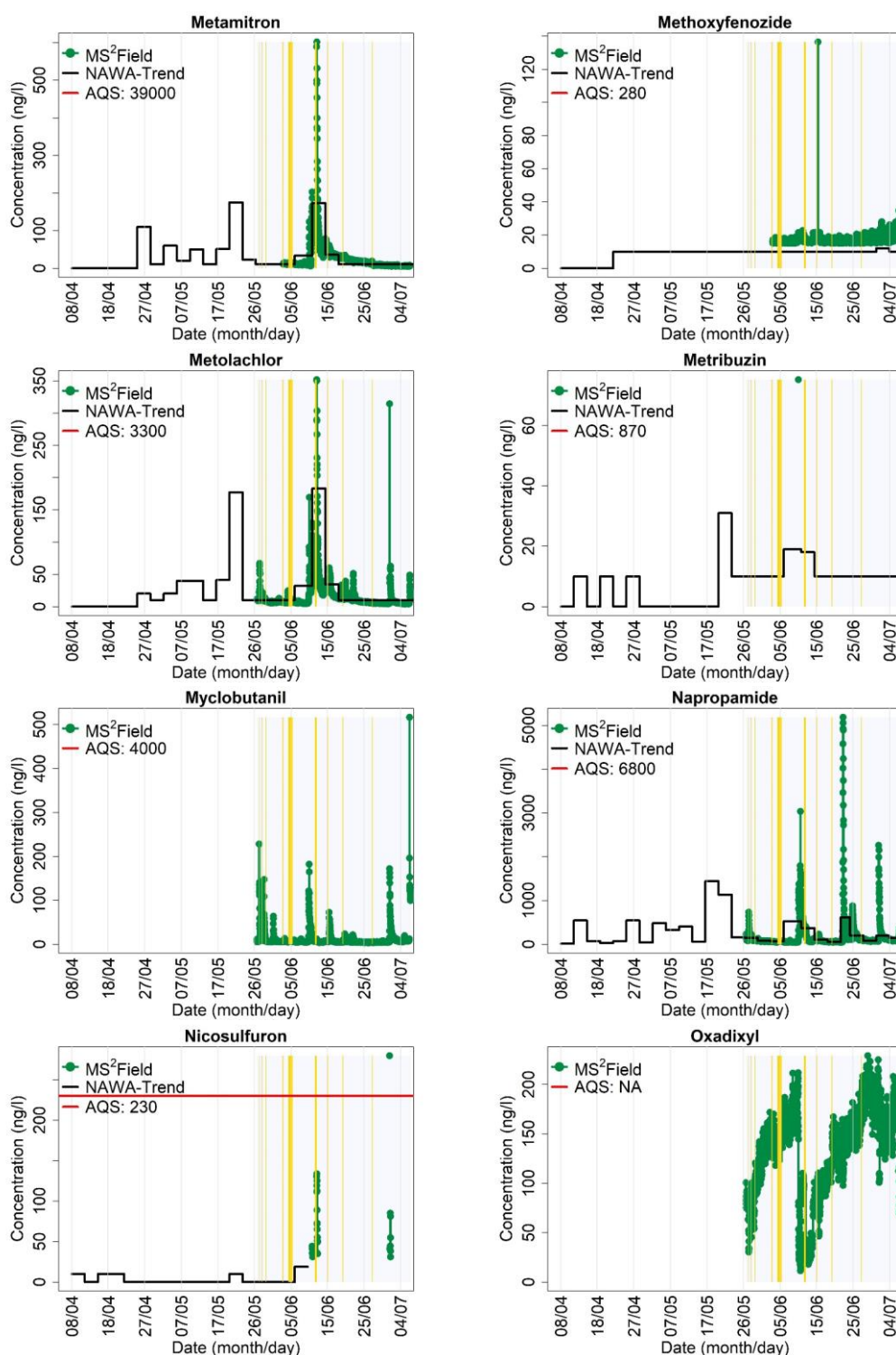
Figure S4: Concentration time series of compounds measured by MS²Field with concentrations above LOQ (green line and bullets). In black, the time series of the compounds that were also measured by NAWA-Trend. MS²Field was used from May 27th to July 7th (light grey background) and NAWA-Trend collected 3.5 days composite samples from April to July. In red, the acute quality standard (AQS). Vertical bars in gold show periods with data gaps due to maintenance of MS²Field.

Figure S5: Concentration time series of compounds measured by MS²Field with concentrations above LOQ (green line and bullets). In black, the time series of the compounds that were also measured by NAWA-Trend. MS²Field was used from May 27th to July 7th (light grey background) and NAWA-Trend collected 3.5 days composite samples from April to July. In red, the acute quality standard (AQS).

Vertical bars in gold show periods with data gaps due to maintenance of MS^{2}Field. Terbutylazin-TP corresponds to terbutylazin desethyl.

Table S7: List of the maximum concentrations reached by the 43 compounds in common between MS^{2}Field and NAWA-TREND. 10 compounds peaked during the MS^{2}Field campaign; 13 compounds peaked before the MS^{2}Field campaign, 7 peaked afterwards and 13 compounds were below LOQ (not shown).

Name	Concentration	Date_st	Date_en
Metalaxyl	10	22.04.2019 07:00	25.04.2019 19:00
Acetamiprid	10	25.04.2019 19:00	29.04.2019 07:00
Cyprodinil	110	02.05.2019 19:00	06.05.2019 07:00
Fenhexamid	500	02.05.2019 19:00	06.05.2019 07:00
Chloridazon	10	06.05.2019 07:00	09.05.2019 19:00
Epoxiconazole	10	09.05.2019 19:00	13.05.2019 07:00
Tebufenozid	60	09.05.2019 19:00	13.05.2019 07:00
Napropamide	1440	16.05.2019 19:00	20.05.2019 07:00
Imidacloprid	29	20.05.2019 07:00	23.05.2019 19:00
Metribuzin	31	20.05.2019 07:00	23.05.2019 19:00
Ethofumesat	110	20.05.2019 07:00	23.05.2019 19:00
Metamitron	175	20.05.2019 07:00	23.05.2019 19:00
Pyrimethanil	202	20.05.2019 07:00	23.05.2019 19:00
Nicosulfuron	19	06.06.2019 15:00	10.06.2019 03:00
Pirimicarb	19	06.06.2019 15:00	10.06.2019 03:00
Fenpyrazamin	650	06.06.2019 15:00	10.06.2019 03:00
Clothianidin	20	11.06.2019 07:00	14.06.2019 19:00
Dimethenamide	31	11.06.2019 07:00	14.06.2019 19:00
Terbutylazine	35	11.06.2019 07:00	14.06.2019 19:00
Metolachlor	183	11.06.2019 07:00	14.06.2019 19:00
Thiamethoxam	28	24.06.2019 06:30	27.06.2019 18:30
Methoxyfenozide	12	01.07.2019 06:00	04.07.2019 18:00
Thiacloprid	274	04.07.2019 18:00	08.07.2019 06:00
Diazinon	16	After July 8th	After July 8th
Diuron	21	After July 8th	After July 8th
DEET	82	After July 8th	After July 8th
Mecoprop	845	After July 8th	After July 8th
Azoxystrobin	1380	After July 8th	After July 8th
Azoxystrobin_free_acid	2440	After July 8th	After July 8th
Fluopyram	5220	After July 8th	After July 8th

Section S7

Positive Matrix Factorization

We used a range of factors from 2 to 13 (i.e. the number of good compounds minus 1). The model was able to accurately model most of the compounds using six to nine factors (Figure S6). The evaluation of the ratio between Qrobust (Q_{robust}) and Qexpected (Q_{exp}) suggests that increasing the number of factors above six does not lead to a strong decrease in the ratio and above eleven the ratio becomes smaller than 1 indicating overfitting (Figure S7). The quality of the solution with a number of factors higher than 6 is improving possibly simply thank to the higher degrees of freedom introduced by the increasing number of factors accounted for. Finally, we notice that the factor profiles of the solutions with a number of factors above six begin to mimic the time series of the target compounds, while do not predict a superposition of the effects as prescribed by the mathematical framework (Figure S8). Given all the above considerations, we decided to retain the solution with six factors (Table S8).

With the selected number of factors, we performed a bootstrap analysis to analyse the quality of the solution. We used the default parameters provided by the software (i.e., $R^2 = 0.6$, block size = 818 data points and number of bootstraps = 100). The mapping between factors and boot factors was generally acceptable because above 70%. The boot factor 2 was matched with factor 1 in less than 10 runs and with factor 5 in less than 20 runs. The non-match could be due to the creation of a block size that does not contain the data points peculiar of the factor. In fact, factors 2 consist of: (1) an early negligible baseline similar to factor 5, (2) a

peculiar response to the large events between June 10th and June 12th, (3) a noisy baseline

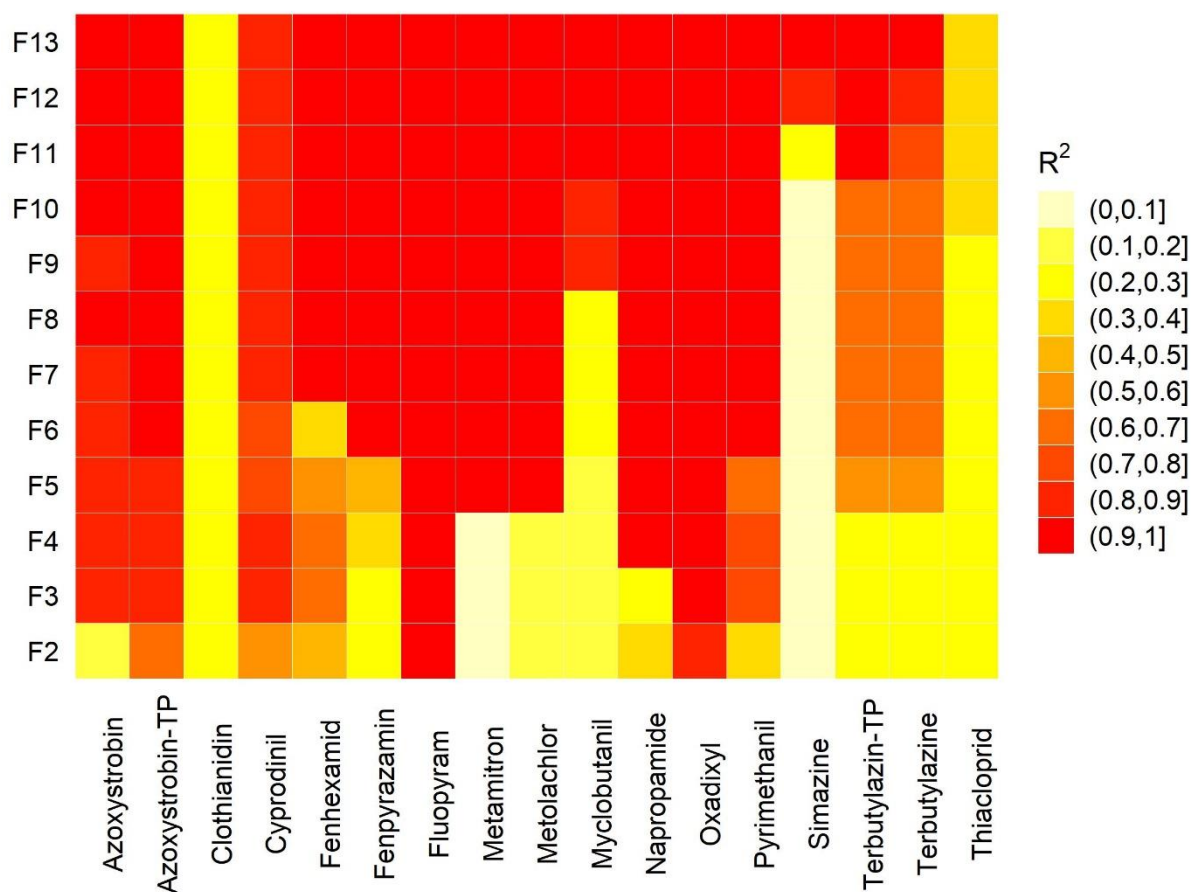similar to factor 1 up to June 23rd and (4) a negligible baseline at the end.

Figure S6: R^2 between measured concentrations and predicted concentrations by the PMF for the different number of factors accounted for. Azoxystrobin-TP corresponds to azoxystrobin free acid and Terbutylazin-TP corresponds to terbutylazin-desethyl.
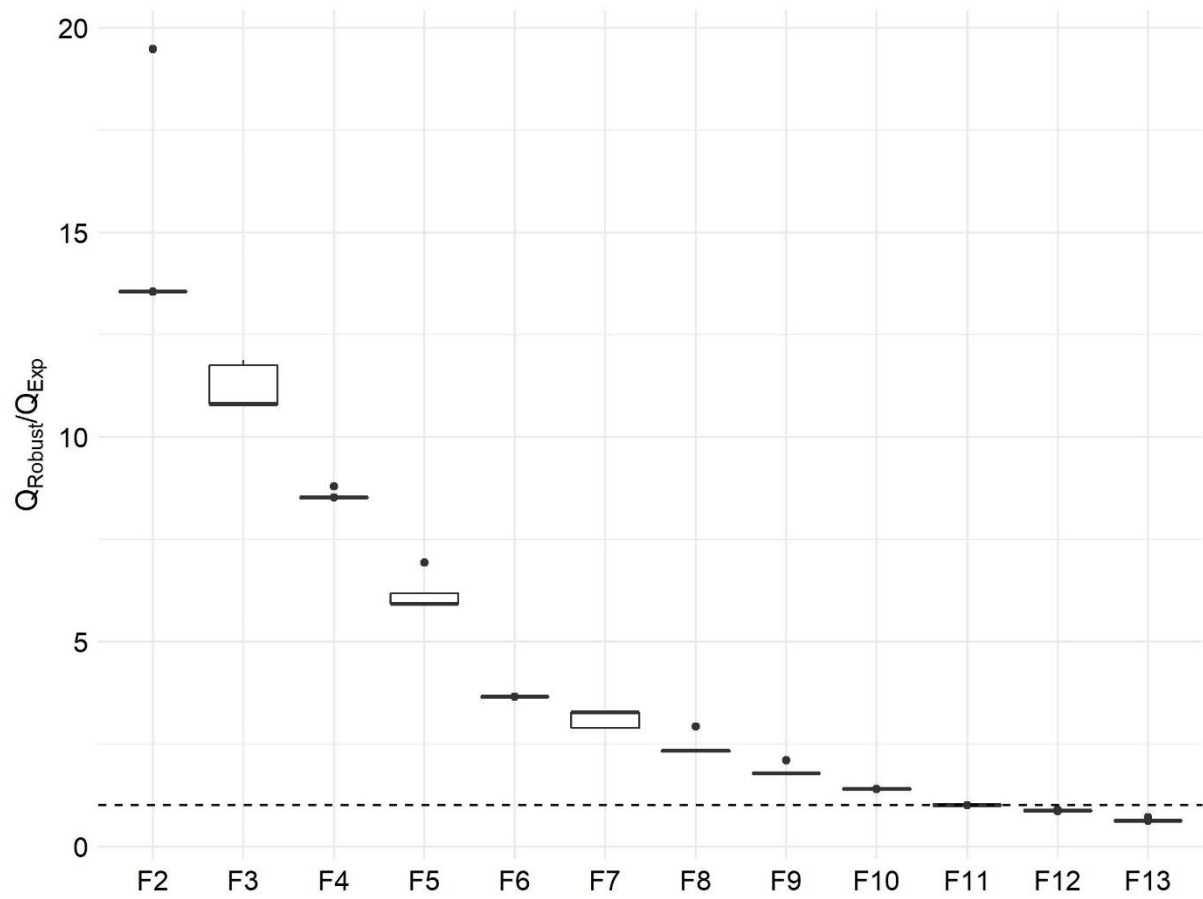
Figure S7: Ratios between Q_{robust} and Q_{exp} for the 20 model runs of each different number of factors accounted for. The dashed line indicates a ratio equal to 1.
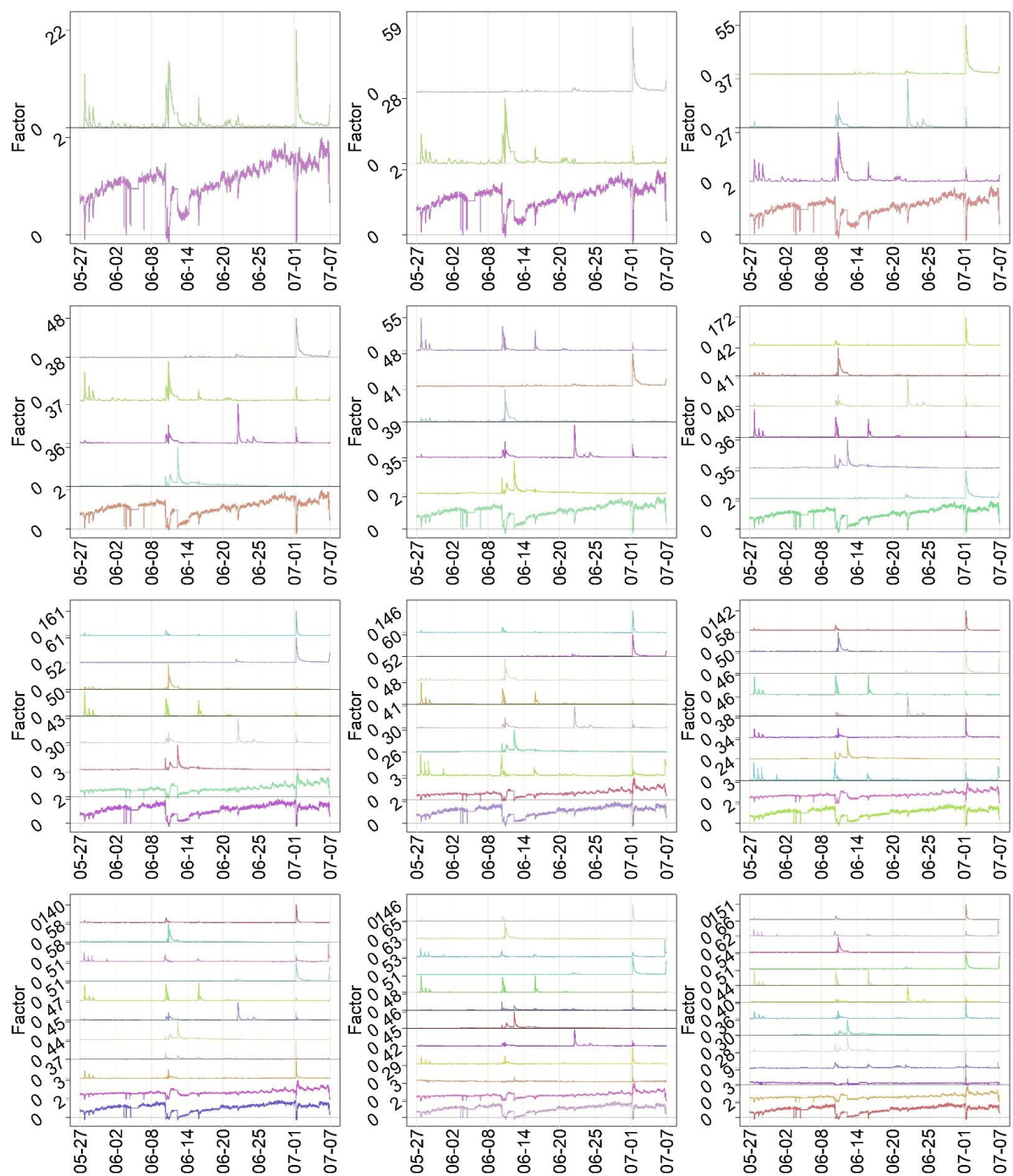
Figure S8: Profiles of the factors for each PMF solution with the range of factors accounted for. x-axis is the date in the format "month-day".

Table S8: Summary of the selected PMF scenario with six factors.

Name	Class	% above LOQ	R^2
Azoxystrobin	Good	97.5	0.84
Azoxystrobin_free_acid	Good	99.8	0.91
Clothianidin	Weak	41.7	0.23
Cyprodinil	Weak	17	0.8
Fenhexamid	Good	37.1	0.36
Fenpyrazamin	Good	100	0.95
Fluopyram	Good	100	0.94
Metamitron	Good	79.3	0.98
Metolachlor	Good	99.4	0.92
Myclobutanil	Good	80.4	0.23
Napropamide	Good	100	1
Oxadixyl	Good	99.4	0.92
Pyrimethanil	Good	72.5	0.93
Simazin	Good	97.2	0.04
Terbutylazine	Good	93	0.63
Terbutylazin_desethyl	Good	99.9	0.62
Thiacloprid	Weak	22.2	0.28
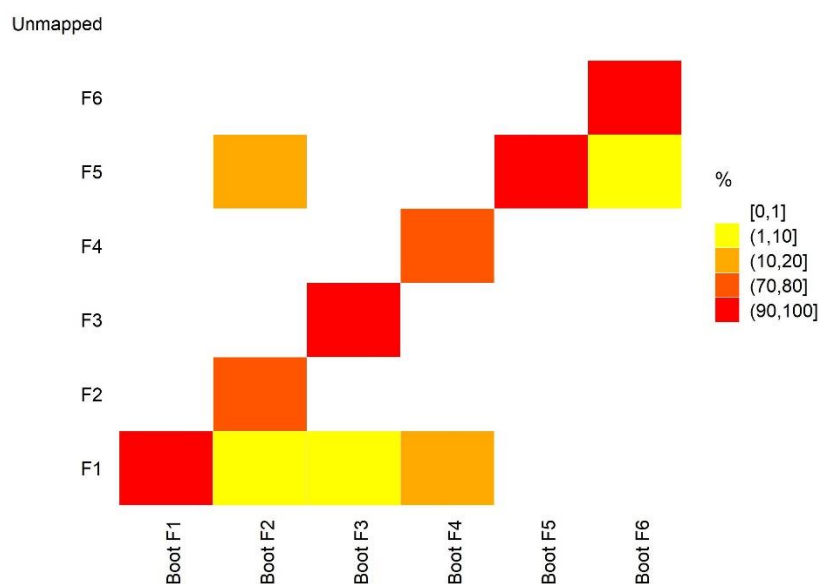
Figure S9: Summary of the bootstrap analysis using the suggested block size of 818 data points and the coefficient of determination R of 0.6. On the x-axis the factors of the bootstrap analysis and on the y-axis the factors of the reference model results.

Section S8

Concentration patterns of different compounds with different properties in different rain events.

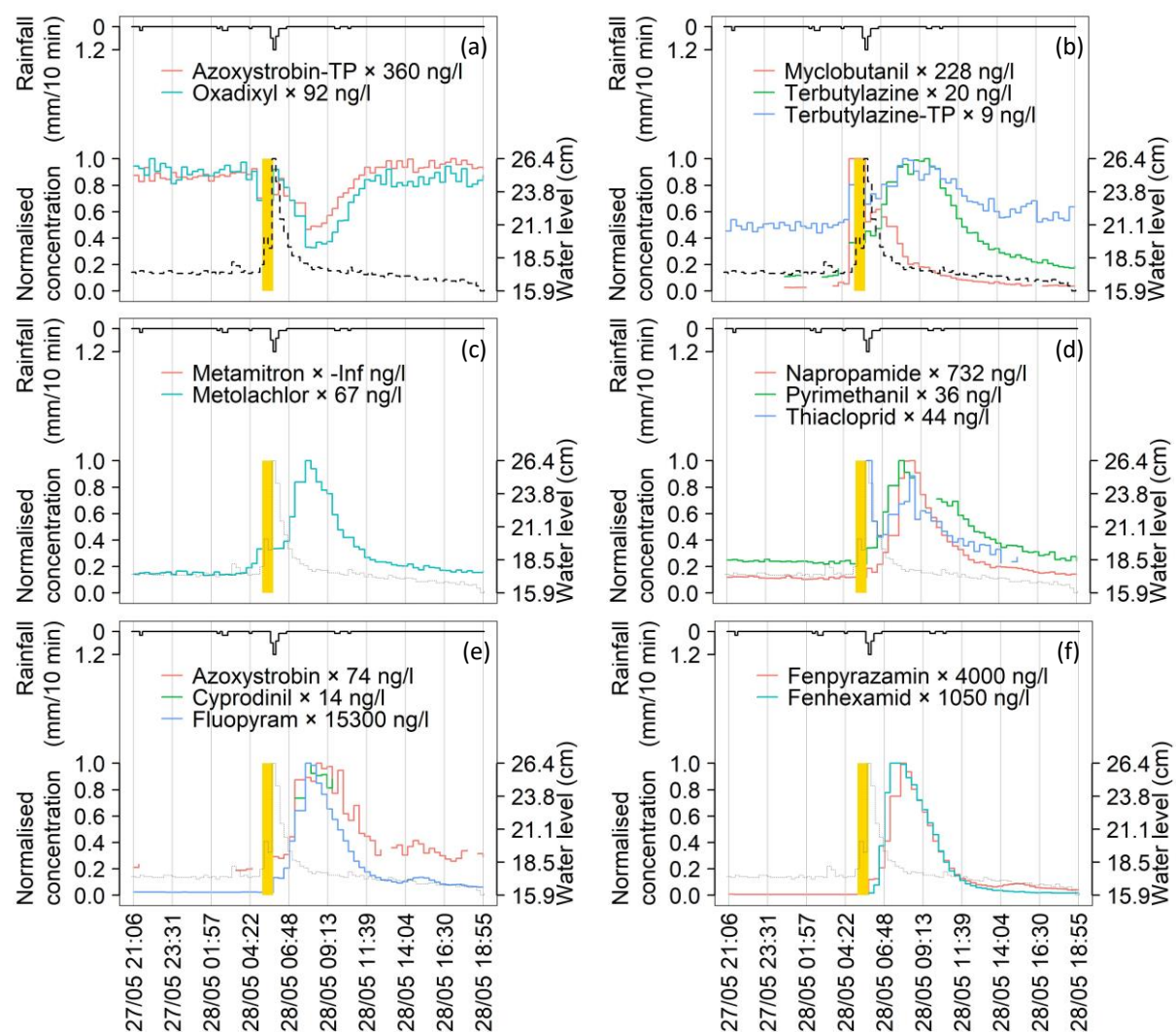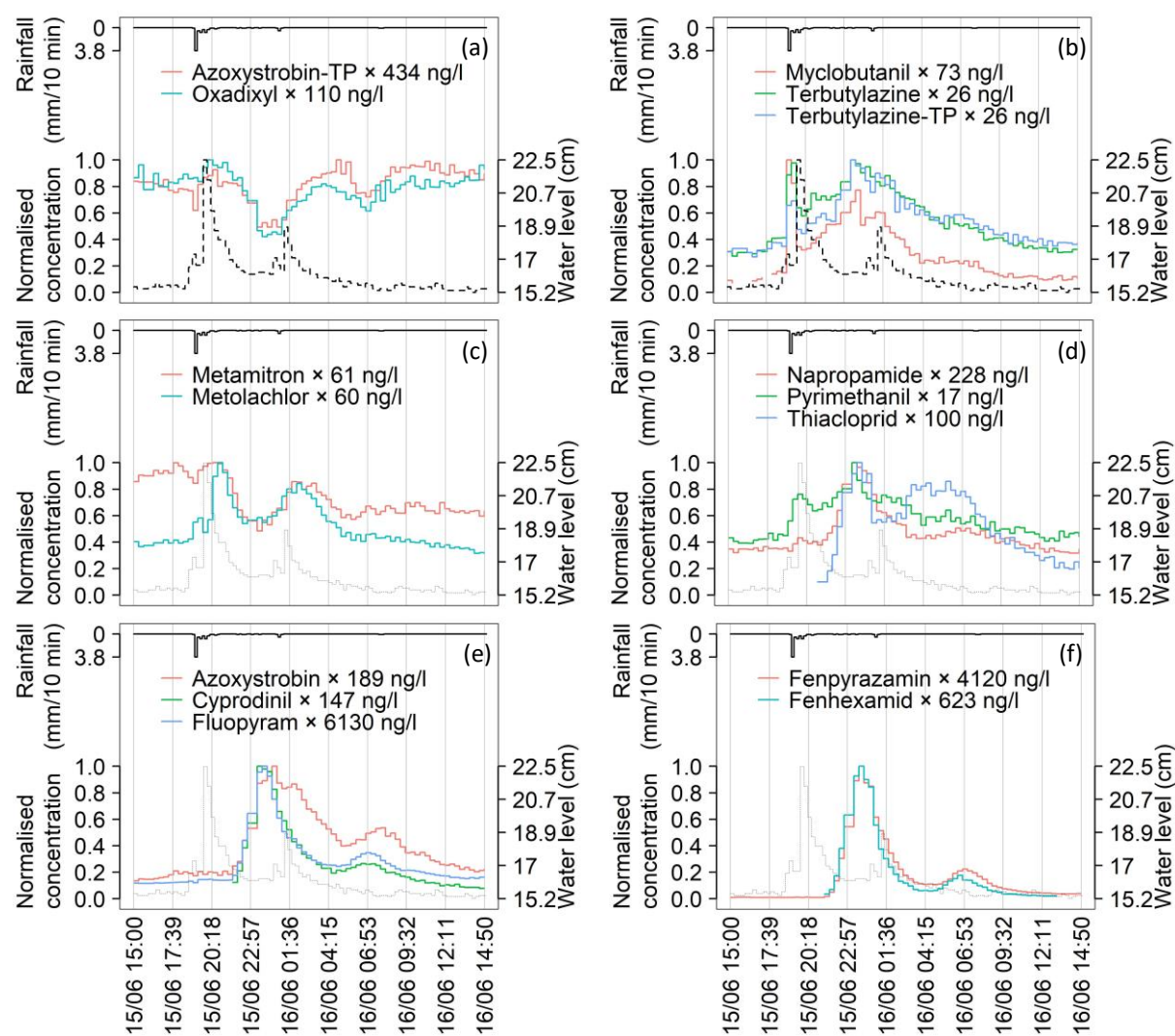**Large event 1: May 28th 2019, 02:20.**

Figure S10: The legend reports the maximum concentrations of each PPPs achieved during the event;

normalised concentration values are represented on the y-axis. Water level as thick black dash line in

(a) and (b) and thin line for readability from (c) to (f). Rainfall as black line on the reversed y-axis.

Vertical bars in gold show periods with data gaps due to maintenance of MS²Field.

Large events 2-3-4: June 10th 2019, 06:00 - June 10th 2019, 10:10 - June 10th 2019, 20:00

(presented in the main manuscript in Figure 3)

Large event 5: June 12th 2019, 01:00 (not captured due to maintenance to MS²Field)

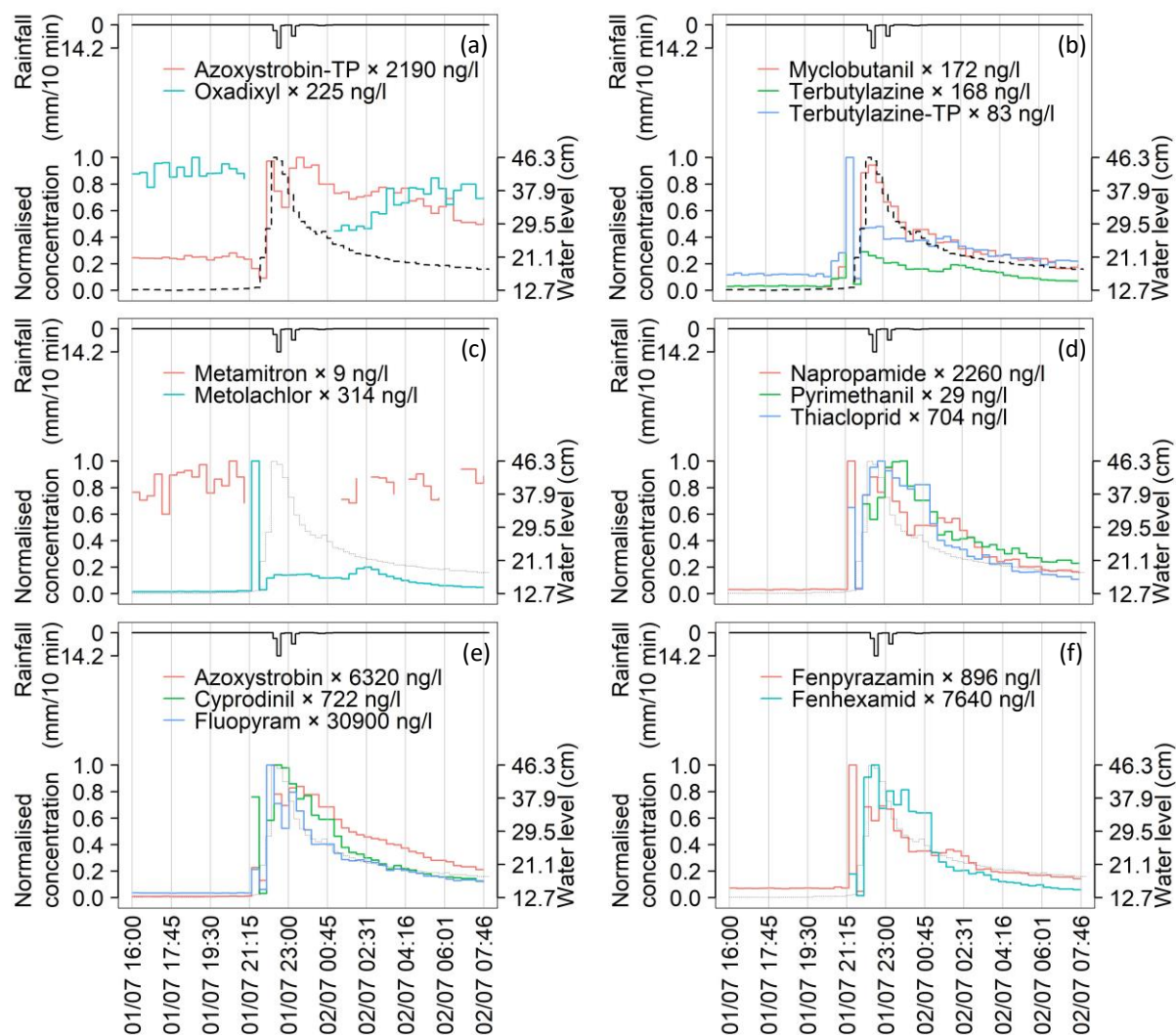**Large event 6: June 15th 2019, 19:00**

Figure S11: The legend reports the maximum concentrations of each PPPs achieved during the event;

normalised concentration values are represented on the y-axis. Water level as thick black dash line in

Large event 7: July 1st 2019, 22:20

Figure S12: The legend reports the maximum concentrations of each PPPs achieved during the event; normalised concentration values are represented on the y-axis. Water level as thick black dash line in (a) and (b) and thin line for readability from (c) to (f). Rainfall as black line on the reversed y-axis. Vertical bars in gold show periods with data gaps due to maintenance of MS²Field.

Large event 6: July 7th 2019, 03:00 (not entirely captured because the monitoring was ended)
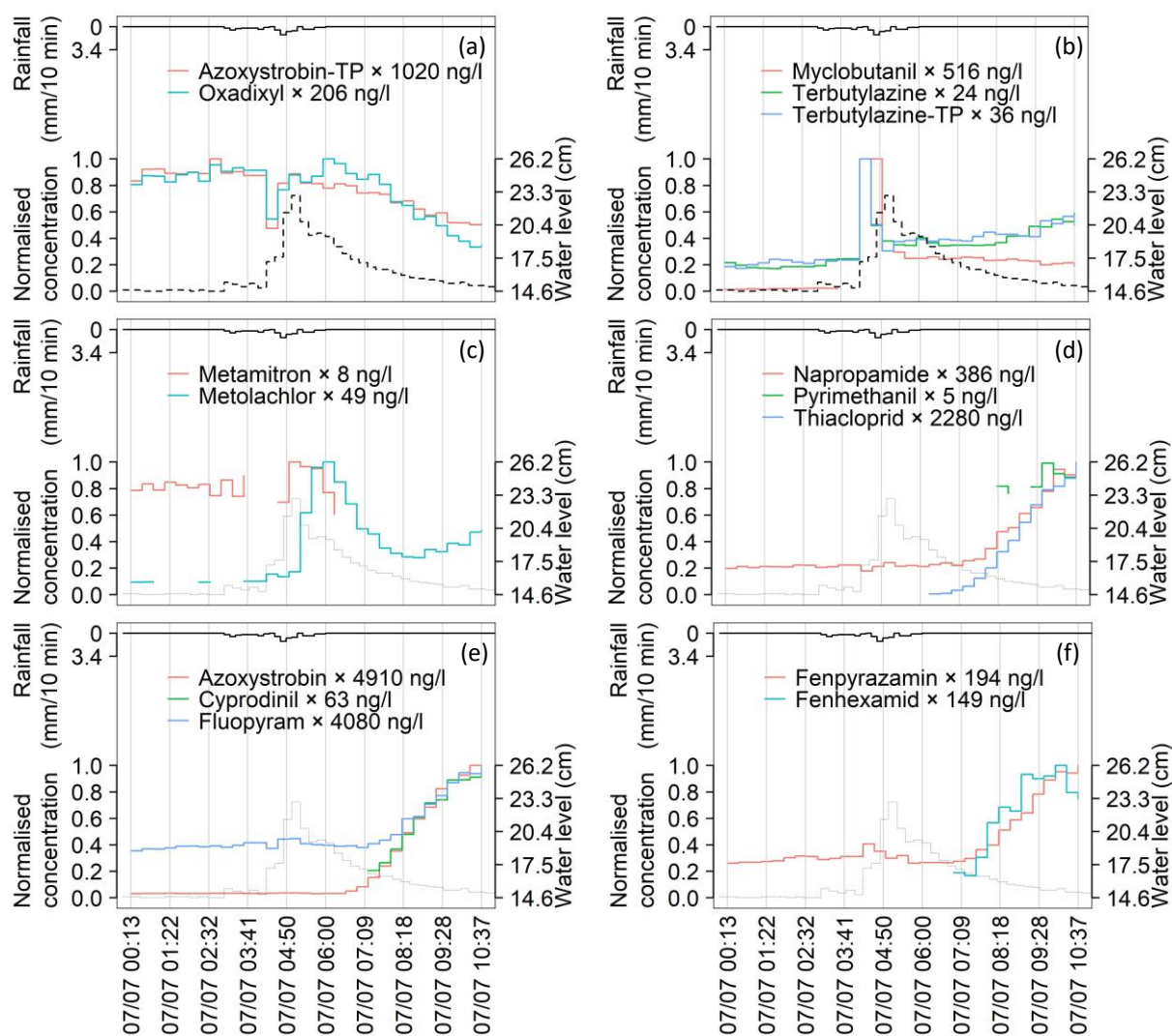
Figure S13: The legend reports the maximum concentrations of each PPPs achieved during the event; normalised concentration values are represented on the y-axis. Water level as thick black dash line in (a) and (b) and thin line for readability from (c) to (f). Rainfall as black line on the reversed y-axis. Vertical bars in gold show periods with data gaps due to maintenance of MS²Field.

Section S9

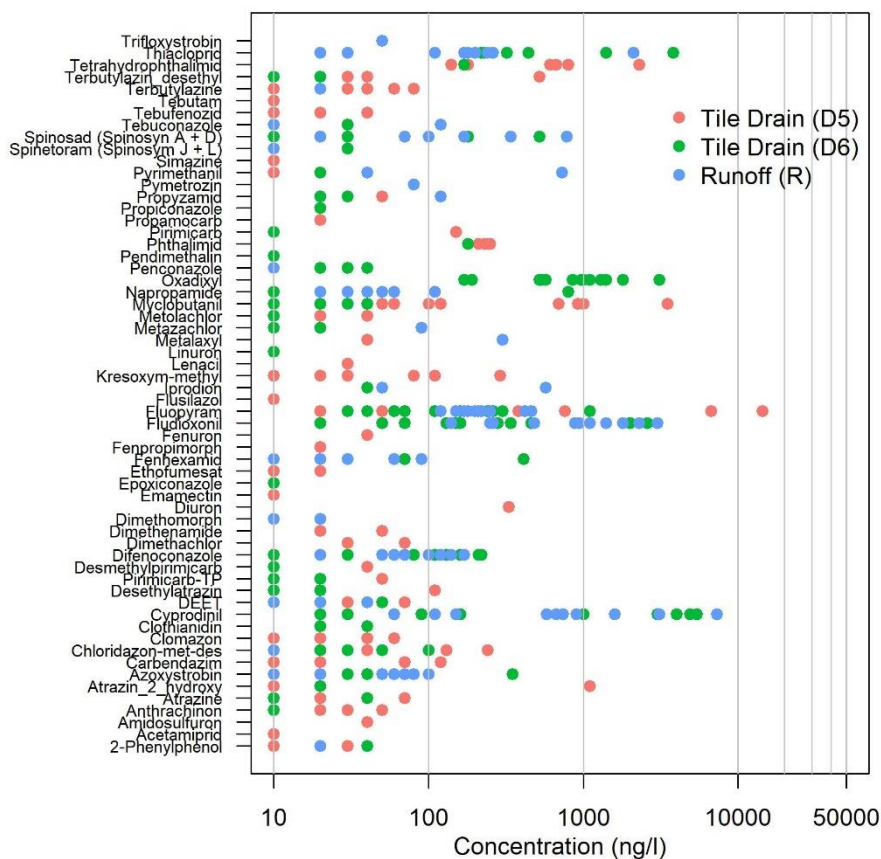## Concentrations in tile drains and runoff over 2019

Figure S14: Concentrations in tile drains and runoff over 2019 (also outside the time window covered with MS^{2}Field).

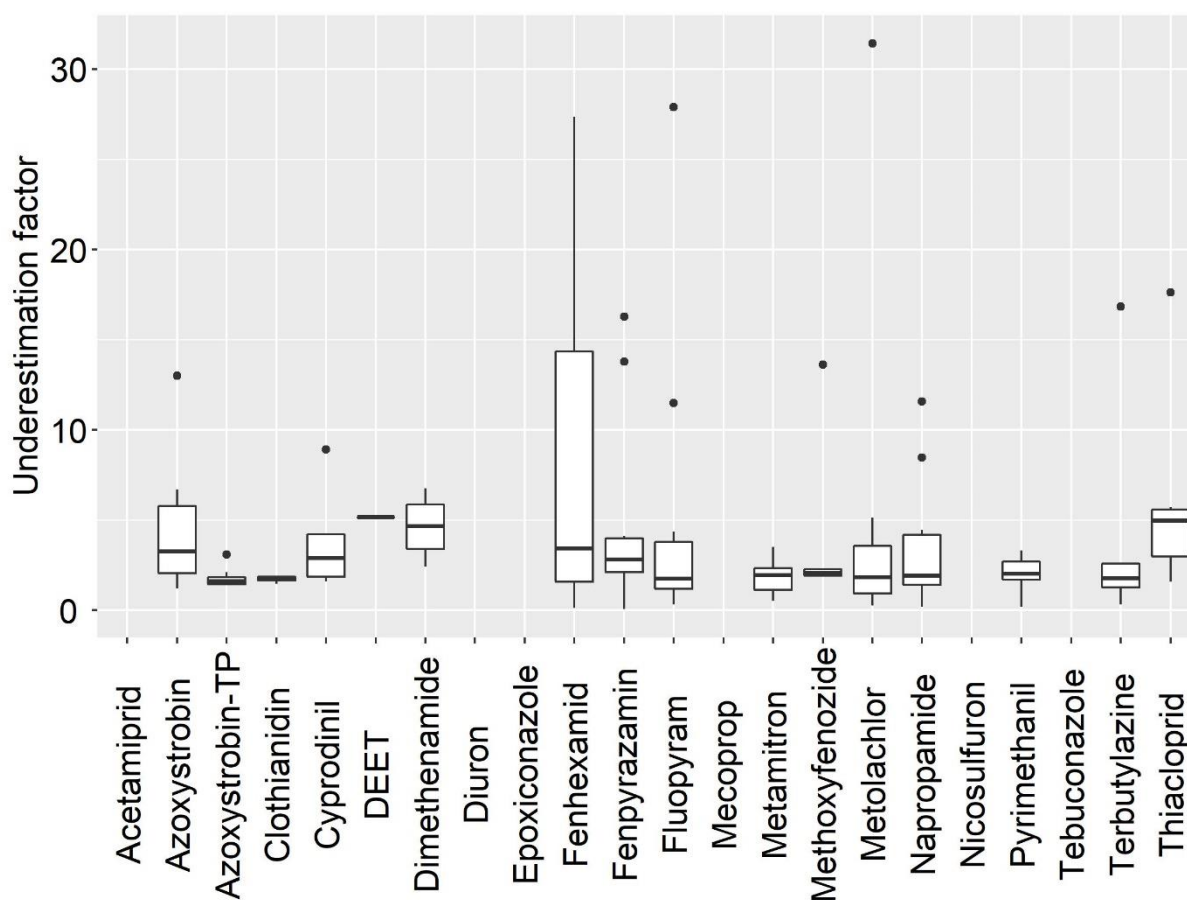# Section S10

Underestimation factor

Figure S15: Underestimation factor calculated as the ratio between the maximum concentration measured by MS^{2}Field and the mean concentration measured by NAWA-Trend in the corresponding 3.5-day composite sample, for all the composite samples collected during the MS^{2}Field campaign. To calculate MS^{2}Field mean concentrations, values below LOQ were set to LOQ and data gaps were disregarded. Azoxystrobin-TP corresponds to azoxystrobin free acid. Compounds with no underestimation factor calculated due to observation of episodic peaks resulting in below LOQ concentratons with extended time composite samples.

Though, different laboratory procedures may yield differences in measured concentrations. Thus, the underestimation factor calculated in Figure S15 may be biased by the different analytical methods of *MS^{2}Field* and the laboratory in Schaffhausen. To highlight potential differences in the measurements, we calculated mean concentrations using the *MS^{2}Field* data relative to the 3.5 days corresponding to

the time-composite samples of NAWA-Trend and we compared this calculated values with the concentrations measured by NAWA-Trend (Figure S16).

Figure S16: Ratio between the mean concentration calculated using the MS²Field measurements and the mean concentration measured by NAWA-Trend in the same 3.5-day composite sample, for all the composite sampled collected during the MS²Field campaign, grouped by compound. To calculate MS²Field mean concentrations, values below LOQ were set to LOQ and data gaps were disregarded. The dashed line indicates a ratio equal to 1. Azoxystrobin-TP corresponds to azoxystrobin free acid.

As expected, often there were small deviations from the ratio of 1 and in few instances, the deviation was substantial. Thus, we inspected the ratio over time for each compound together with an error propagation analysis. To this aim, we assigned the measurement error quantified by the laboratory in Schaffhausen for each compound to all concentration data points for the

corresponding compound measured in the context of NAWA-Trend. The error for each compound measured by *MS²Field* was calculated as in Section S4.

When calculating the mean over 3.5 days using *MS²Field*, we are summing the measurements and dividing by the number of data points. Being A_i the measurement at time t_i for a given compound up to *n* with n being the number of times, the sum $X = \sum_n A_n$ will have an error U_X = nU_A. The division Y= X/n, with Y being the mean over a time window, will have an error U_Y = U_X/n.

Now, Z is the measured concentration in the NAWA-Trend program, with a measured error U_Z.

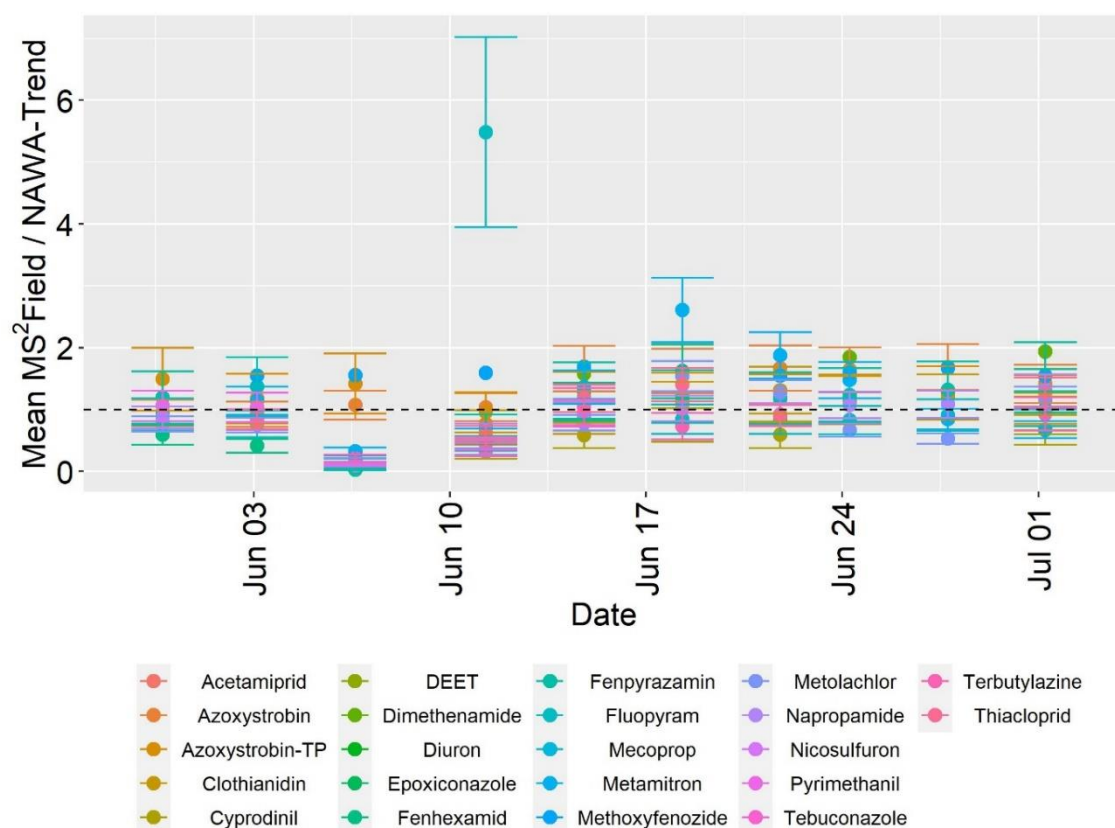Finally, the error of the ratio R=Y/Z will have an error U_R = R*(U_Y*Y + U_Z*Z).

Figure S17: Error propagation analysis of the ratio between the mean concentration calculated using the MS²Field measurements and the mean concentration measured by NAWA-Trend in the same 3.5-

day composite sample, for all the composite sampled collected during the MS²Field campaign, grouped by time. To calculate MS²Field mean concentrations, values below LOQ were set to LOQ and data gaps were disregarded. The dashed line indicates a ratio equal to 1. Azoxystrobin-TP corresponds to azoxystrobin free acid.

The error in the measurements can explain the small deviations from a value of the ratio close to 1. Azoxystrobin was systematically overestimated, while cyprodinil was underestimated. This may be due to the corresponding recoveries, of 140% for azoxystrobin and of 60% for cyprodinil. But few substantial deviations remained. This is because in the interval between June 6 and June 10, the NAWA-Trend measurement were largely higher than the calculated mean concentrations of *MS²Field*. While relative to June 6, the reason is not known, in June 10, *MS²Field* had an issue and did not collect water samples for several hours during a large rain event, which is expected to drive high concentration peaks for several compounds (e.g., fluopyram). The NAWA-Trend measurements indicate that we very likely missed a concerning pollution event.

Section S11

Acknowledging the limitations highlighted in Section S10, we calculated 3.5-days mean concentrations using the MS^2Field measurements, starting from the beginning of the MS^2Field monitoring campaign. This allowed for:

(i) considering measurements in the period between June 10th at 07:00 and June 11th at 19:00 when NAWA-Trend was not operational;

(ii) Running a sensitivity analysis where we shifted the starting point of the resampling by 20 minutes until a complete shift of 3.5 days was reached to avoid repetitions (note that in this way we discarded concentration data up to 3.5 days after the beginning of MS^2Field monitoring, which however was not a concerning period in terms of concentration peaks).
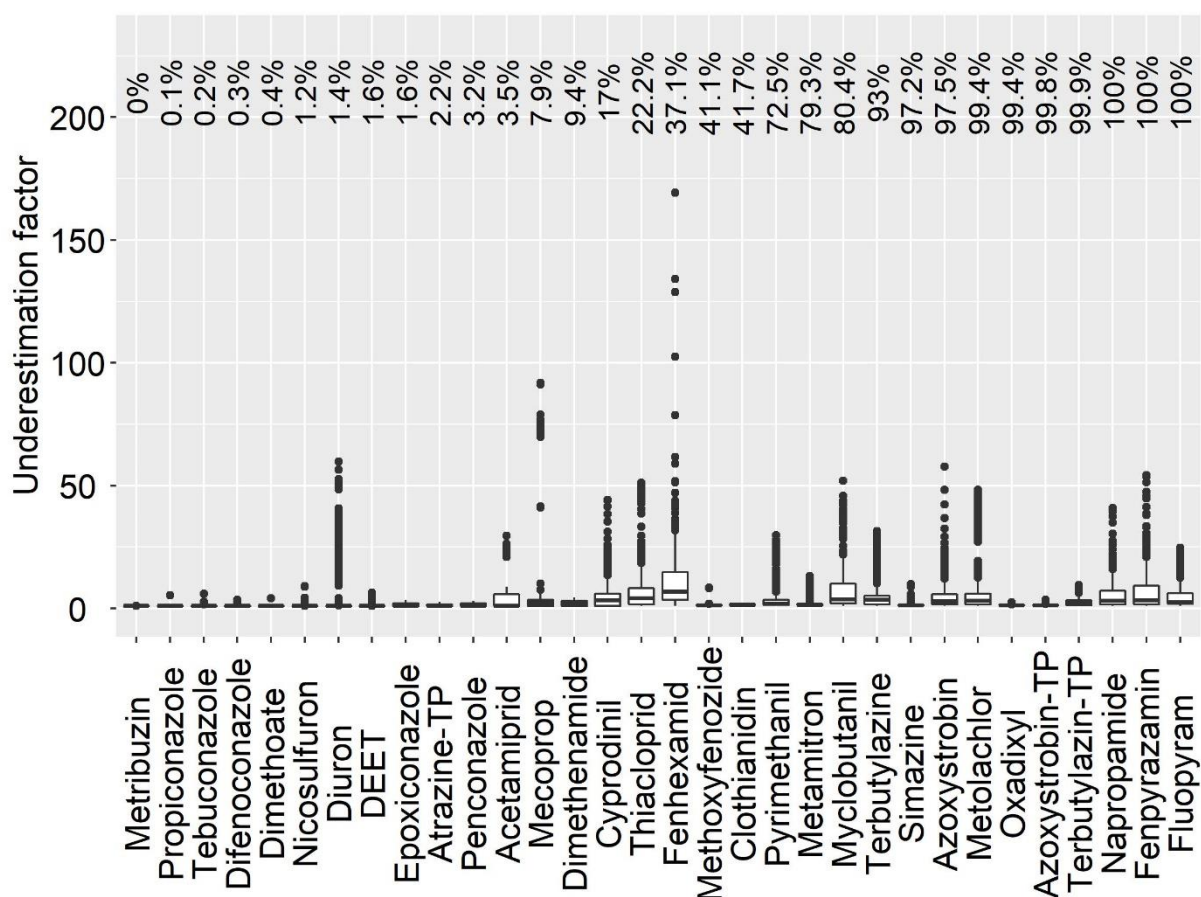
Figure S18: Numerical underestimation factor calculated considering time composite samples of 3.5 days. Compounds sorted by the percentage of detections during the MS²Field monitoring (percentages, excluding data gaps, reported above the boxplots). Atrazine-TP corresponds to atrazine desethyl desisopropyl, Azoxystrobin-TP corresponds to azoxystrobin free acid and Terbutylazin-TP corresponds to terbutylazin desethyl.

We repeated the analysis by calculating mean concentrations over 14 days as this is the standard in other stations part of the Swiss national monitoring program.
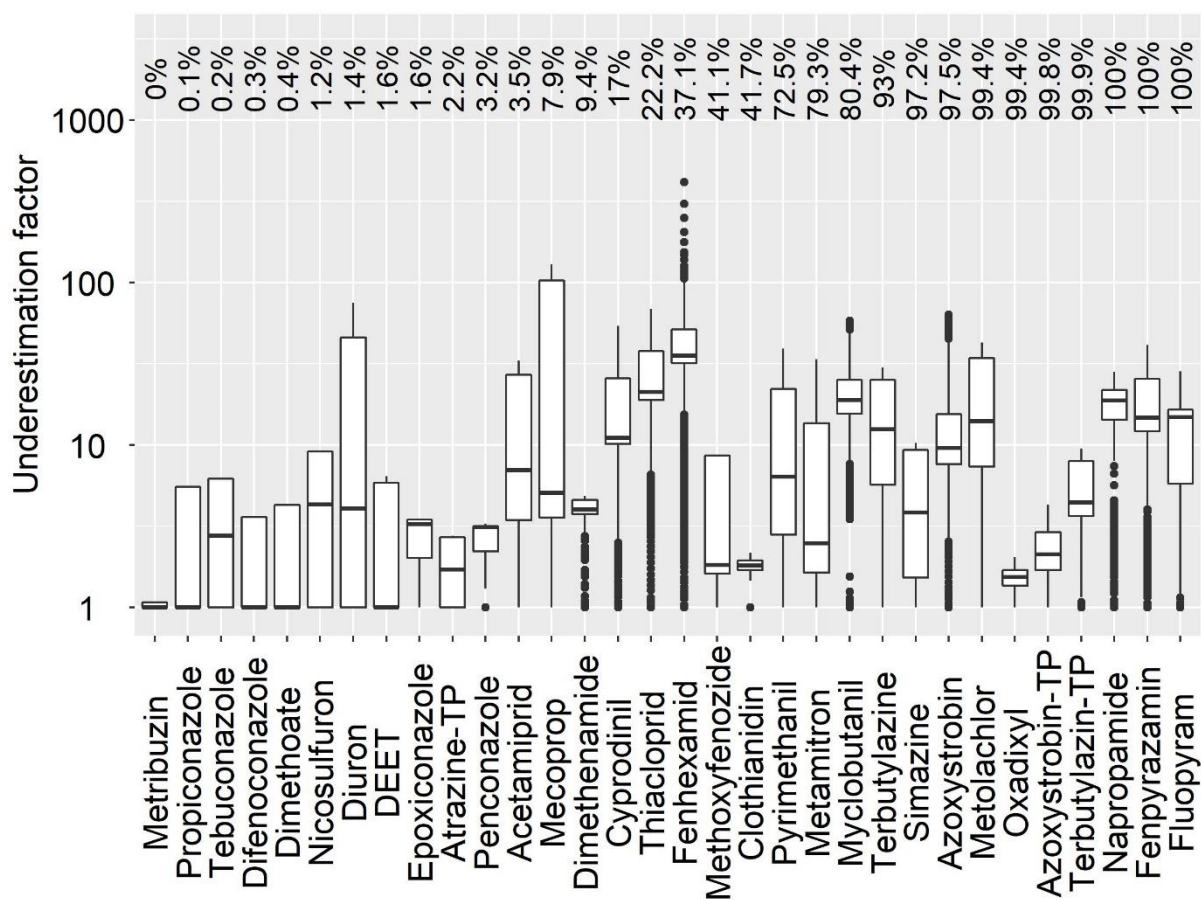
Figure S19: Numerical underestimation factor calculated considering time composite samples of 14 days. Compounds sorted by the percentage of detections during the MS²Field monitoring (percentages, excluding data gaps, reported above the boxplots). Atrazine-TP corresponds to atrazine desethyl desisopropyl, Azoxystrobin-TP corresponds to azoxystrobin free acid and Terbutylazin-TP corresponds to terbutylazin desethyl.

Section S12

Comprehensive acute and chronic exposure assessment. We performed the water quality assessment against acute quality standards (AQS) and chronic quality standards (CQS) currently

reported in the Swiss legislation. An assessment based on chronic exposure only would had underestimated the risk given that during the 14 days when we registered with MS^2Field the 5 AQS exceedances reported in Table S9, only 2 CQS exceedances occurred. In particular, azoxystrobin exceeded its CQS but not its AQS, while thiacloprid exceeded both standards. We further noted that the chronic exposure to nicolfuron could not be quantified given the high LOQ of both methods (i.e., LOQ by MS^2Field is 30 ng/l and LOQ by NAWA-Trend is 11 ng/l, respectively reported in Table S1 and *Table S2*).

Table S9: Measured maximum concentrations during AQS exceedances according to MS^2Field (MS^2Field), measured time composite concentrations of 3.5 days in the Swiss monitoring program (NAWA-Trend 3.5 days) and calculated time composite samples of 14 days using the NAWA-Trend data (NAWA-Trend 14 days). Calculated composite concentration as mean concentration of MS^2Field measurements over the corresponding 3.5-days interval (indicated with *) and 14-days interval (indicated with **) used in NAWA-Trend for compounds not measured in NAWA Trend in that period (concentration values < LOQ set to LOQ and the neglected missing samples for quality checks purposes amounted to ≈10% within the time intervals). NA stands for PPPs not measured by MS^2Field. Concentrations at 20 minutes and 3.5 days resolution compared against AQS (pale yellow background), while concentrations at 14 days resolution compared against CQS (light blue background). Quality standards exceedances in bold. ***: LOQ>CQS, therefore the risk assessment was not reliable.

Compound	Time stamp	*MS^2Field* (ng/l)	NAWA-Trend 3.5 days (ng/l)	NAWA-Trend 14-days (ng/l)	AQS (ng/l)	CQS (ng/l)	Underestimation factor for 3.5-days (-)	Underestimation factor for 14-days (-)
Azoxystrobin	July 1st	**≈6300**	≈490	**≈360**	550	200	12.8	17.5
Diuron	July 7th	**≈490**	<LOQ (15)	<LOQ (15)	250	70	>32.6	>32.6

Fluopyram	July 1st	**≈30900**	≈2690	≈1860	25100	13500	11.4	16.6
Nicosulfuron	July 1st	**≈280**	*≈32	**≈30	230	8.7***	*8.8	**9.2
Thiacloprid	July 7th	**≈2280**	≈270	**≈78**	80	10	8.3	28.9
Carbendazim	May 2nd - May 6th	NA	**≈790**	≈250	700	440	-	-
Chlorpyrifos-methyl	May 9th - May 13th	NA	**≈10**	**≈2.5**	7.3	1	-	-

Section S13

Figure S20: Images from the satellite Sentinel-2 show the potential for identifying spatial-temporal dynamics of plastic tunnels.