Supporting information for

Continuous high-frequency pesticide concentrations in a small agricultural stream to reveal the overlooked and the unexpected in dry periods

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Section S1

Land use change between 2019 and 2020

The Swiss land use map with resolution at the spatial level encompassed 37 different categories (Source: Swiss Federal Office of Topography). These classes were grouped into 11 macrocategories according to Table S1.

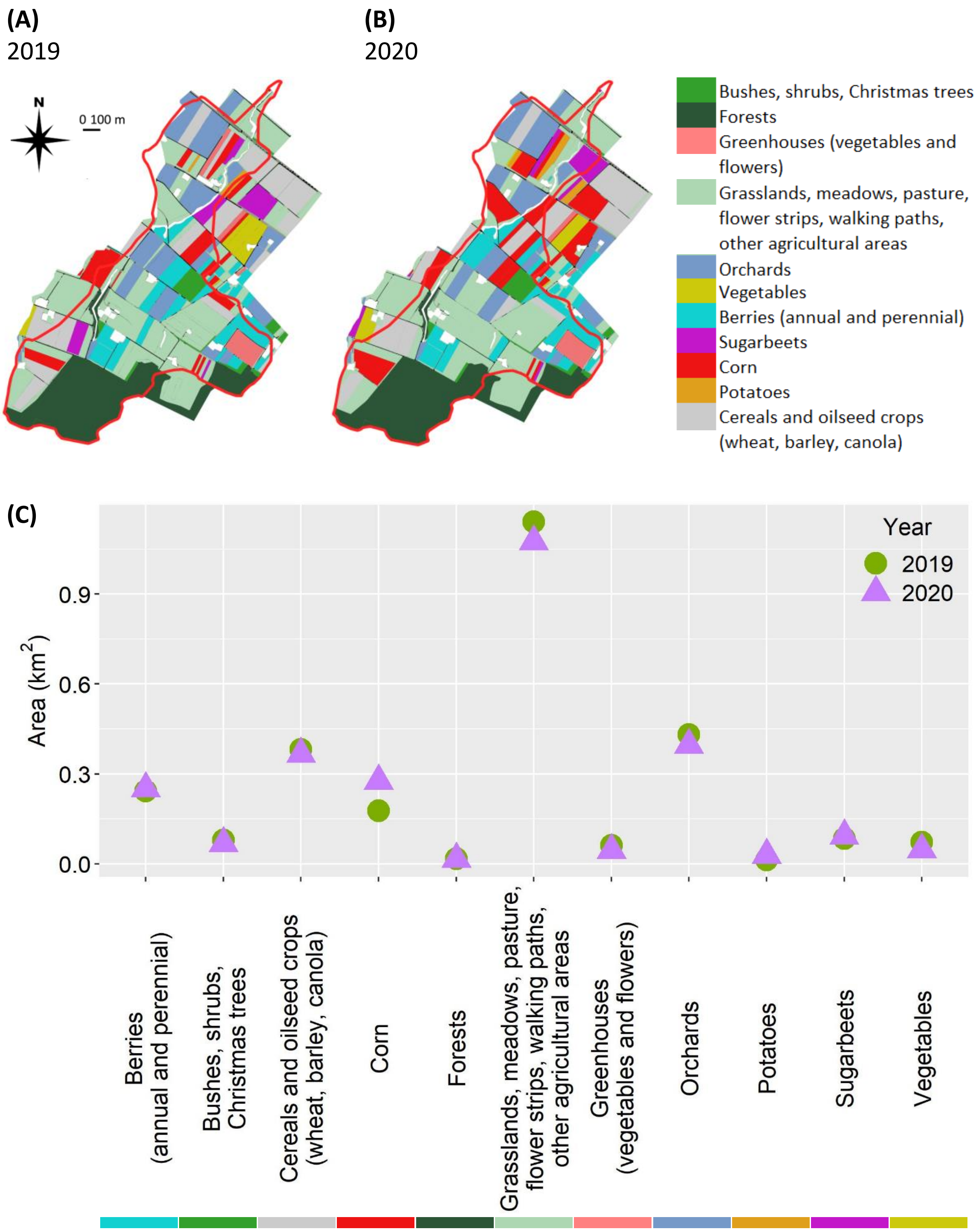

Figure S1: Land use in (A) 2019, (B) 2020 and (C) quantitative changes between 2019 and 2020. Land use in 2019 was firstly published gold open access in la Cecilia et al., 2021.

Table S1: Conversion from original land use name to the corresponding macrocategory.

Name land use	Name macrocategory
Bushes	Bushes, shrubs, Christmas trees
Shrubs	Bushes, shrubs, Christmas trees
Christmas trees	Bushes, shrubs, Christmas trees
Forests	Forests
Vegetables in greenhouse without foundations	Greenhouses (vegetables and flowers)
Special crops in greenhouse without foundations	Greenhouses (vegetables and flowers)
Forcing houses	Greenhouses (vegetables and flowers)
Floriculture in greenhouse without foundations	Greenhouses (vegetables and flowers)
Floriculture	Greenhouses (vegetables and flowers)
Grasslands	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Meadows	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Pasture	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Other agricultural areas	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Other agricultural areas	Green areas
Meadows	Green areas
Pasture	Green areas
Flower strips	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Walking paths	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Other agricultural areas	Grasslands, meadows, pasture, flower strips, walking paths, other agricultural areas
Apple orchard	Orchards
Pear orchard	Orchards
Other orchards	Orchards
Asparagus	Vegetables
Vegetables	Vegetables
Strawberries	Berries (annual and perennial)
Perennial berries	Berries (annual and perennial)
Sugarbeet as forage	Sugarbeets
Sugarbeet	Sugarbeets
Corn	Corn
Corn as ensilage	Corn
Potatoes	Potatoes

Wheat as forage	Cereals and oilseed crops (wheat, barley, canola)
Autumn wheat	Cereals and oilseed crops (wheat, barley, canola)
Barley	Cereals and oilseed crops (wheat, barley, canola)
Canola for oil	Cereals and oilseed crops (wheat, barley, canola)

Section S2

Sampling locations

Figure S2: Photos of the sampling locations. Samples taken by the author DLC (in the pictures) and the colleagues Birgit Beck and Reynold Chow. Photos taken by Reynold Chow.

Section S3

Analytical chemistry relative to the dry-day field campaign of August 12th, 2020

Table S2: List of target compounds with corresponding LOQ values and relative recovery.

Name	Name in manuscript	Detected	LOQ (ng/l)	Relative Recovery (%)
Aldicarb	Aldicarb	No	20	89
Diazinon	Diazinon	No	5	69
Dimethenamid-P	Dimethenamide	No	5	82
Diuron	Diuron	No	5	87
Thiacloprid	Thiacloprid	No	5	88
Azoxystrobin	Azoxystrobin	Yes	9	73
Azoxystrobin free acid	Azoxystrobin-TP	Yes	10	97
Clothianidin	Clothianidin	Yes	5	87
Fenpyrazamin	Fenpyrazamin	Yes	5	112
Fluopyram benzamide	Fluopyram-TP	Yes	5	109
Fluopyram	Fluopyram	Yes	8	42
Metamitron	Metamitron	Yes	9	92
Napropamide	Napropamide	Yes	9	74
Oxadixyl	Oxadixyl	Yes	10	91
Simazine	Simazine	Yes	6	83

Table S3: List of target compounds with corresponding relative standard deviation among three replicates greater than 10%.

Name in manuscript	Location	Time	Mean concentration	Standard deviation	Relative standard deviation (%)
Clothianidin	ES1	6	20	2.2	11.3
Clothianidin	ES2	6	8	1.7	21.2
Clothianidin	ES2	18	7	1.3	17.5
Clothianidin	ES4	6	11	2.5	21.4
Clothianidin	ES4	12	12	2.1	18.0
Clothianidin	ES4	22	10	2.2	23.3
Clothianidin	ES5	6	9	2.6	27.9
Clothianidin	ES5	18	10	1.0	10.2
Clothianidin	ES6	6	9	1.2	13.9
Clothianidin	ES6	12	11	1.5	13.9
Clothianidin	ES6	18	10	1.3	13.0
Fenpyrazamin	ES2	12	10	1.0	10.5
Fenpyrazamin	ES2	18	12	1.6	13.3
Fenpyrazamin	ES4	18	7	2.3	31.2
Fenpyrazamin	ES4	22	8	1.8	23.0

Fenpyrazamin	ES5	22	7	1.6	21.9
Fluopyram-TP	ES1	6	49	5.8	11.9
Fluopyram-TP	ES1	12	53	5.3	10.0
Fluopyram-TP	ES3	6	29	3.2	11.3
Oxadixyl	ES6	12	187	18.9	10.1
Simazine	ES1	6	11	1.4	13.4
Simazine	ES1	12	8	0.9	10.8
Simazine	ES1	18	8	1.0	12.8
Azoxystrobin-TP	TD2	22	380	41.0	11.8
Azoxystrobin-TP	TD3	18	34	4.2	13.3
Azoxystrobin-TP	TD4	12	394	43.5	10.7
Fluopyram-TP	TD3	12	6	0.7	11.1
Fluopyram-TP	TD4	18	8	0.9	10.1
Oxadixyl	TD3	12	184	18.4	10.6
Oxadixyl	TD4	12	47	5.4	11.4
Simazine	TD1	18	12	1.5	15.0

Section S4

Time series of water levels and concentrations measured by MS2Field for the compounds that exceeded their LOQ in the dry periods.

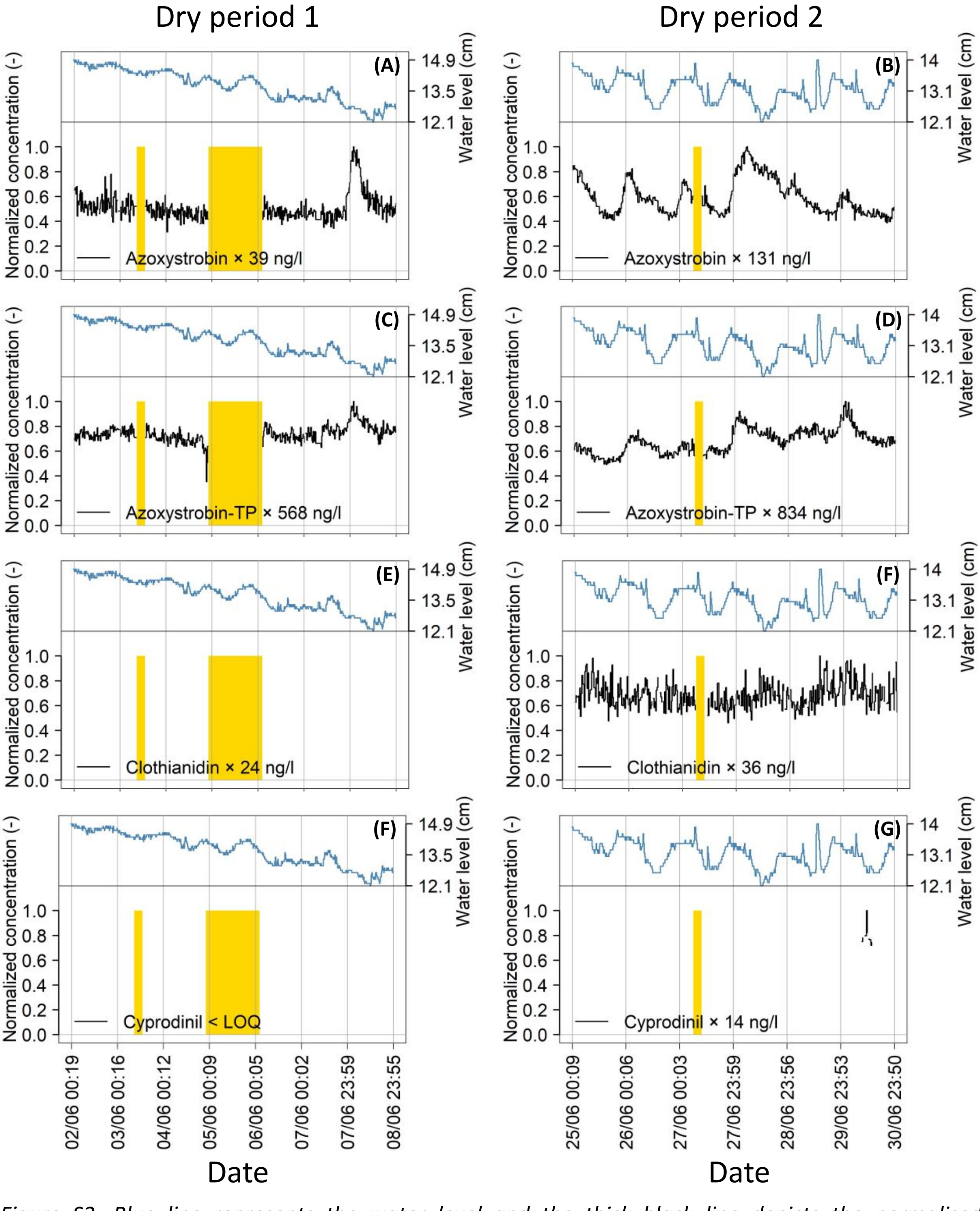

Figure S3: Blue line represents the water level and the thick black line depicts the normalised concentration time series of compounds measured by MS²Field with concentrations above LOQ (maximum concentration value per compound is written in the legend). Vertical bars in gold show periods with data gaps due to maintenance of MS²Field. Panels on the left correspond to the first dry period from June 2nd to June 8th 2019. Panels on the right correspond to the second dry period from June 25th to June 30th 2019.

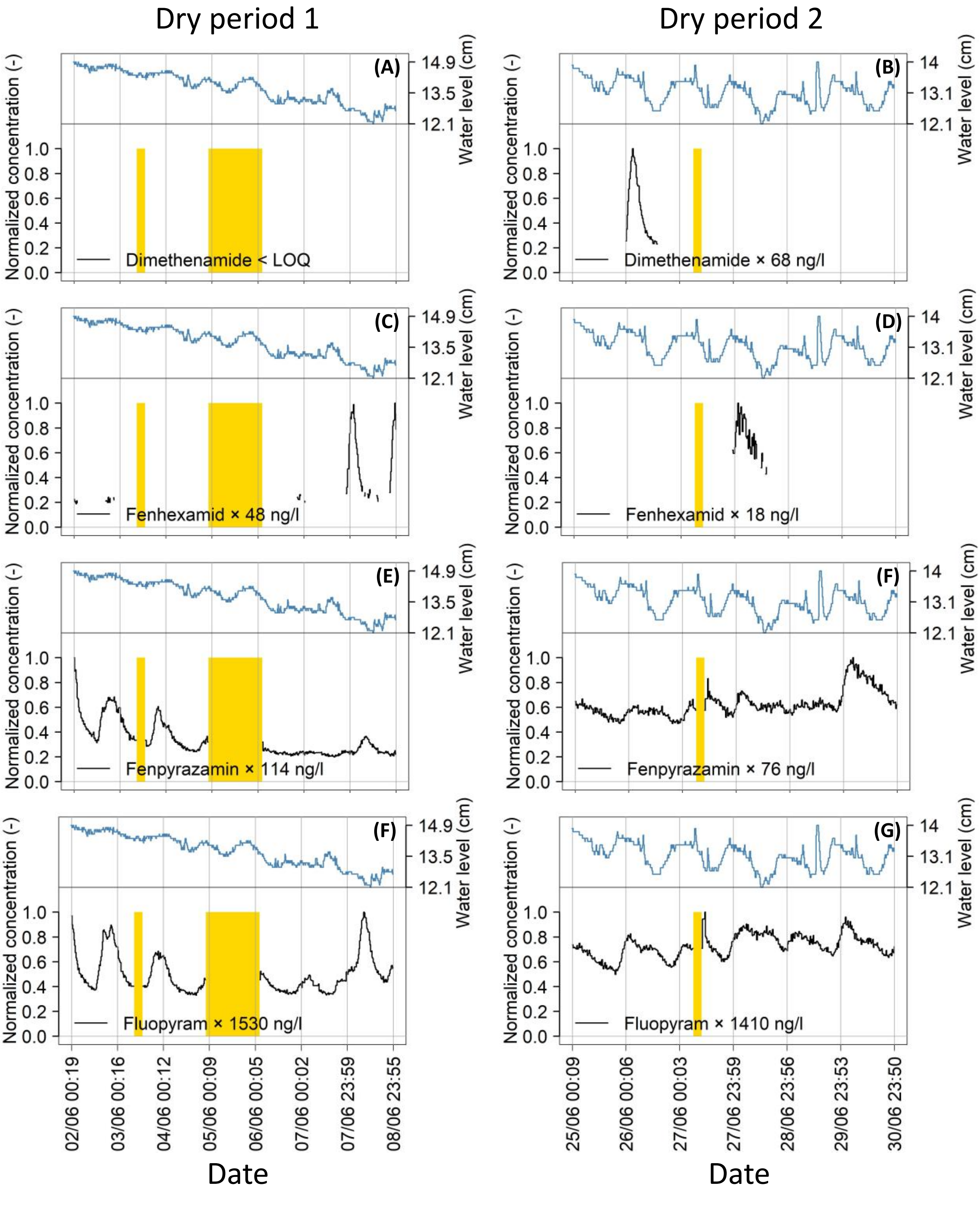

Figure S4: Blue line represents the water level and the thick black line depicts the normalised concentration time series of compounds measured by MS^{2}Field with concentrations above LOQ (maximum concentration value per compound is written in the legend). Vertical bars in gold show periods with data gaps due to maintenance of MS^{2}Field. Panels on the left correspond to the first dry period from June 2nd to June 8th 2019. Panels on the right correspond to the second dry period from June 25th to June 30th 2019.

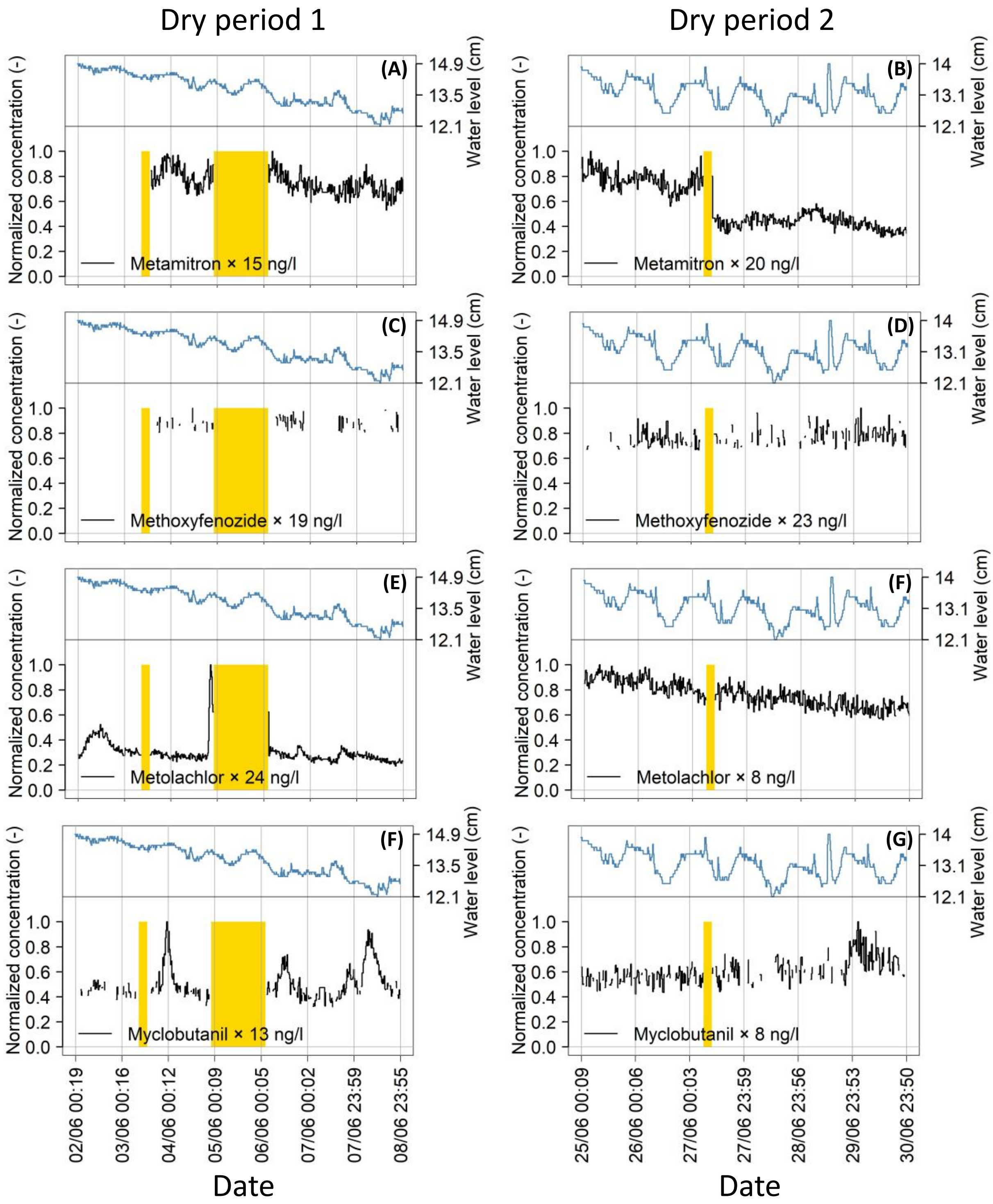

Figure S5: Blue line represents the water level and the thick black line depicts the normalised concentration time series of compounds measured by MS^{2}Field with concentrations above LOQ (maximum concentration value per compound is written in the legend). Vertical bars in gold show periods with data gaps due to maintenance of MS^{2}Field. Panels on the left correspond to the first dry period from June 2nd to June 8th 2019. Panels on the right correspond to the second dry period from June 25th to June 30th 2019.

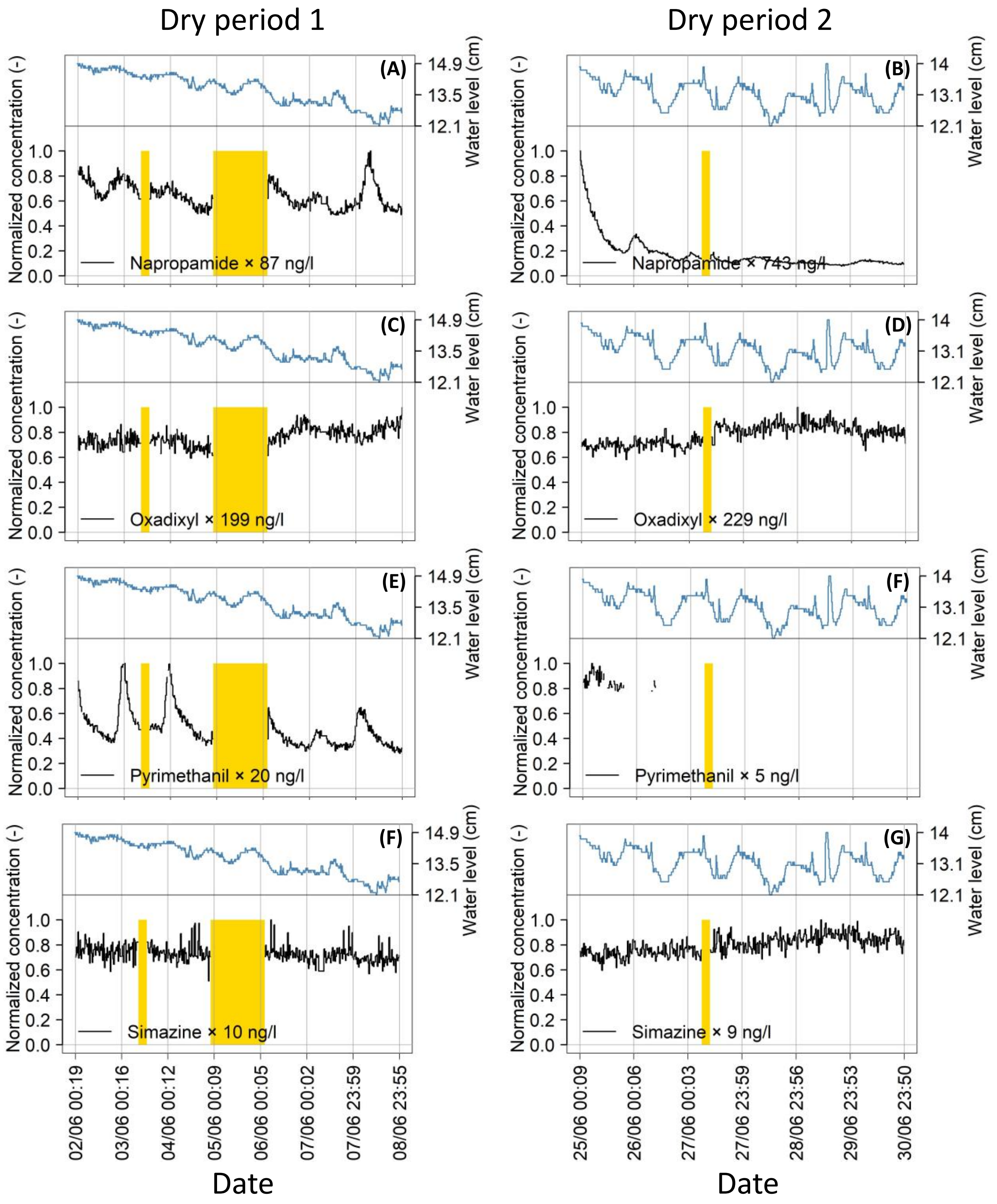

Figure S6: Blue line represents the water level and the thick black line depicts the normalised concentration time series of compounds measured by MS²Field with concentrations above LOQ (maximum concentration value per compound is written in the legend). Vertical bars in gold show periods with data gaps due to maintenance of MS²Field. Panels on the left correspond to the first dry period from June 2nd to June 8th 2019. Panels on the right correspond to the second dry period from June 25th to June 30th 2019.

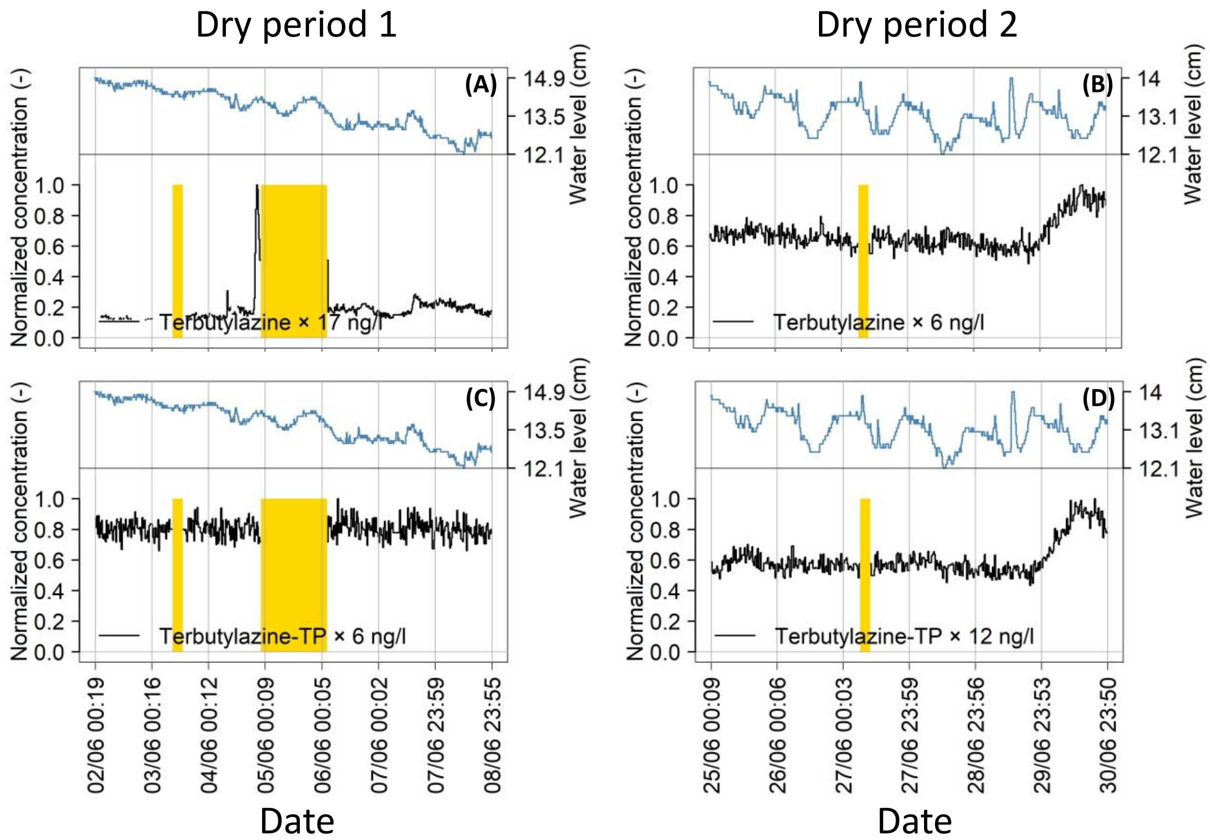

Figure S7: Blue line represents the water level and the thick black line depicts the normalised concentration time series of compounds measured by MS^{2}Field with concentrations above LOQ (maximum concentration value per compound is written in the legend). Vertical bars in gold show periods with data gaps due to maintenance of MS^{2}Field. Panels on the left correspond to the first dry period from June 2nd to June 8th 2019. Panels on the right correspond to the second dry period from June 25th to June 30th 2019.

Section S5

Analysis of lagged correlations

We calculated the Pearson correlation coefficient (*r*) between the concentration (*C*) time series, and the water level (*WL*) time series, with *r* defined as $r(\Delta t) = \frac{cov(WL(t+\Delta t),C(t))}{\sigma_{WL(t+\Delta t)}\sigma_{C(t)}}$ to include a lag time Δt. The range of Δt spanned 1 day with a step equal to the temporal resolution of *MS²Field* (i.e., 20 minutes). To calculate *r*, first we had to linearly interpolate the water levels at 15 minutes resolution to the sampling times of *MS²Field*.

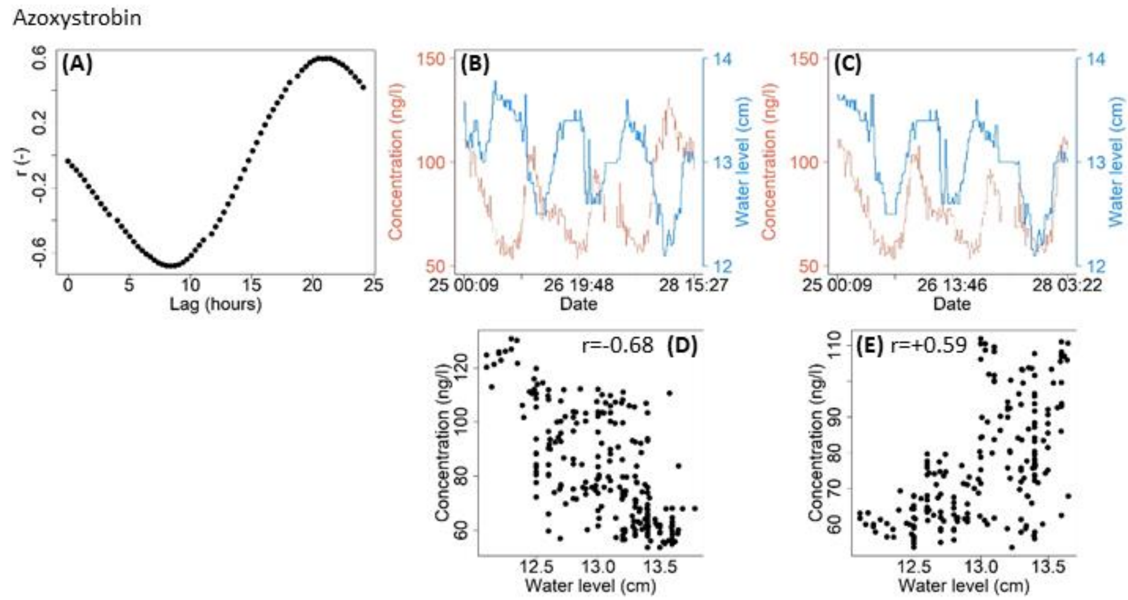

Figure S8: Lagged-correlation analysis for Azoxystrobin. ***(A)*** *values of r as a function of the lag time Δt.* ***(B)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈8 hours, which resulted in the minimum r (negative correlation).* ***(C)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈20 hours, which resulted in the maximum r (positive correlation).* ***(D)*** *Scatter plot between water levels and concentration values as in panel* ***(B)****.* ***(E)*** *Scatter plot between water levels and concentration values as in panel* ***(C)****.*

Azoxystrobin-TP

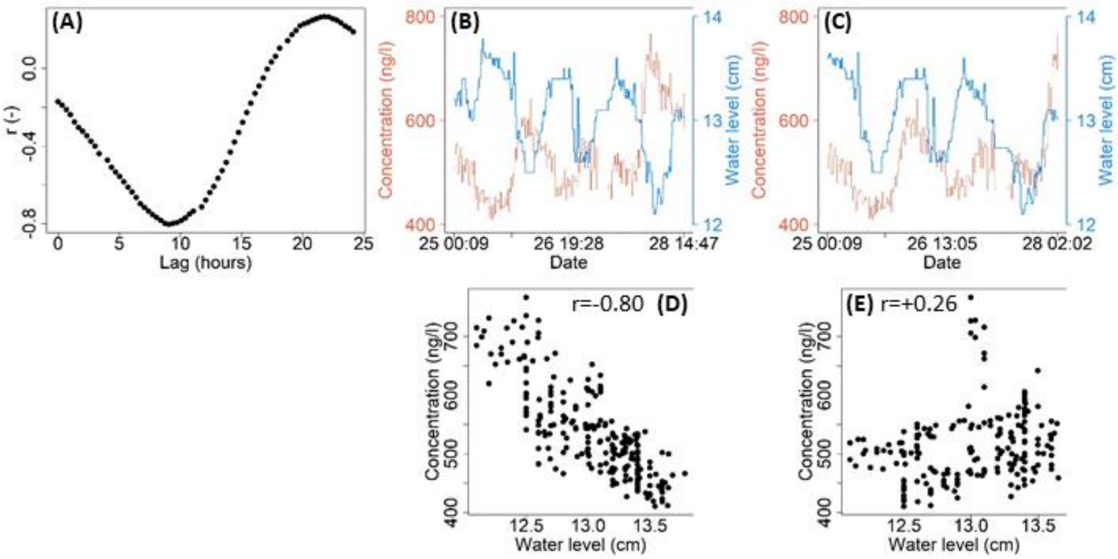

Figure S9: Lagged-correlation analysis for Azoxystrobin free acid (Azoxystrobin-TP). ***(A)*** *values of r as a function of the lag time Δt.* ***(B)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈9 hours, which resulted in the minimum r (negative correlation).* ***(C)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈22 hours, which resulted in the maximum r (positive correlation).* ***(D)*** *Scatter plot between water levels and concentration values as in panel* ***(B)***. ***(E)*** *Scatter plot between water levels and concentration values as in panel* ***(C)***.

Fenpyrazamin

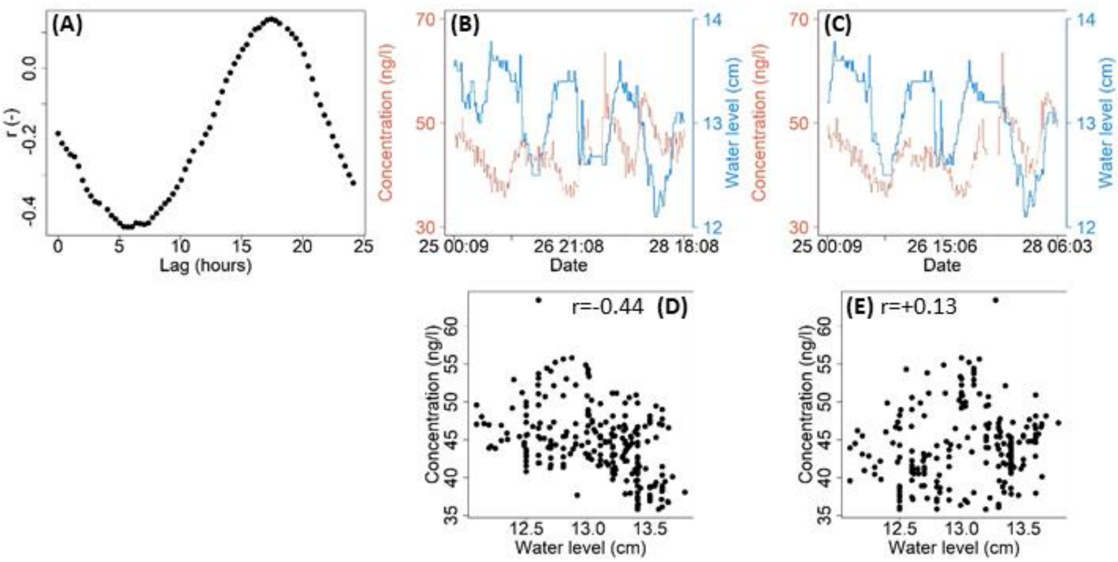

Figure S10: Lagged-correlation analysis for Fenpyrazamin. ***(A)*** *values of r as a function of the lag time Δt.* ***(B)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈6 hours, which resulted in the minimum r (negative correlation).* ***(C)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈17 hours, which resulted in the maximum r (positive correlation).* ***(D)*** *Scatter plot between water levels and concentration values as in panel* ***(B)***. ***(E)*** *Scatter plot between water levels and concentration values as in panel* ***(C)***.

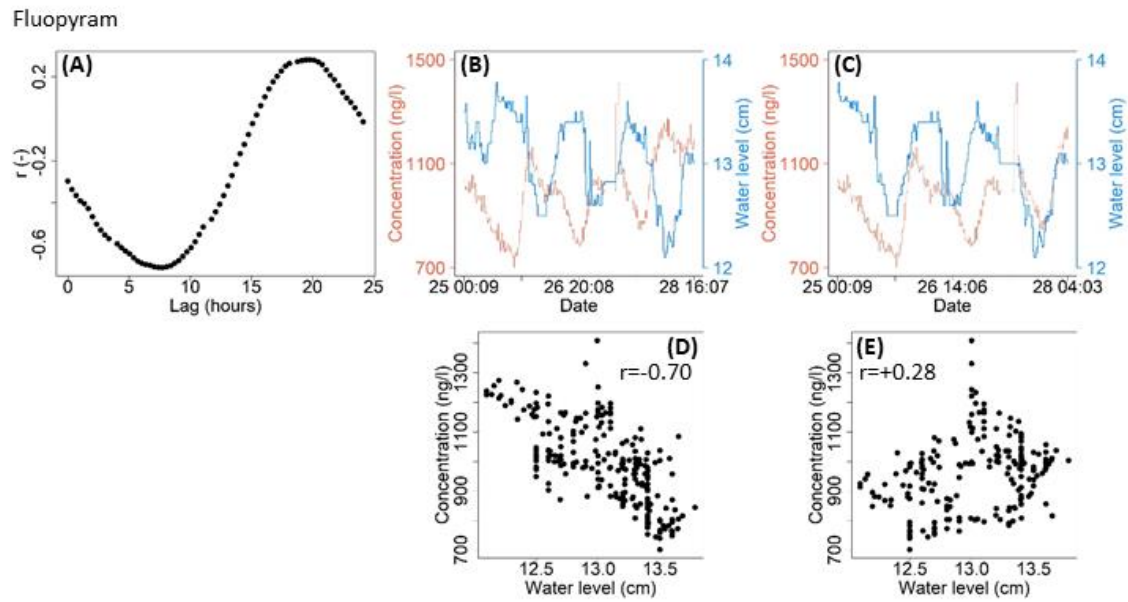

Figure S11: Lagged-correlation analysis for Fluopyram. ***(A)*** *values of r as a function of the lag time Δt.* ***(B)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈8 hours, which resulted in the minimum r (negative correlation).* ***(C)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈20 hours, which resulted in the maximum r (positive correlation).* ***(D)*** *Scatter plot between water levels and concentration values as in panel* ***(B)****.* ***(E)*** *Scatter plot between water levels and concentration values as in panel* ***(C)****.*

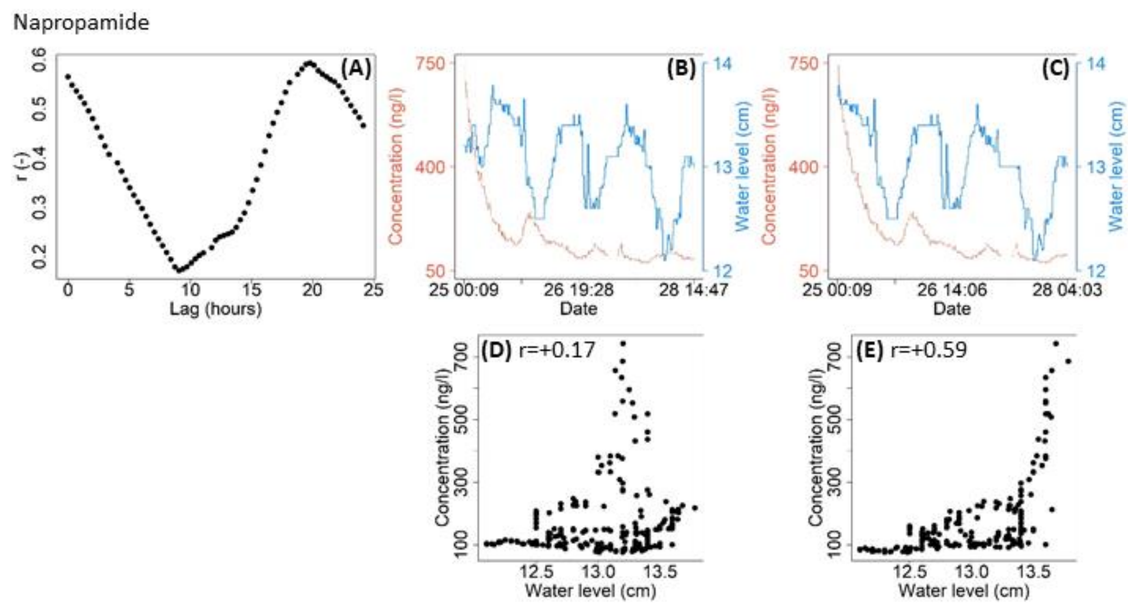

Figure S12: Lagged-correlation analysis for Napropamide. ***(A)*** *values of r as a function of the lag time Δt.* ***(B)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈9 hours, which resulted in the minimum r (negative correlation).* ***(C)*** *Time series of water levels and concentration values given a delay to the water levels of Δt≈20 hours, which resulted in the maximum r (positive correlation).* ***(D)*** *Scatter plot between water levels and concentration values as in panel* ***(B)****.* ***(E)*** *Scatter plot between water levels and concentration values as in panel* ***(C)****.*

Section S6

Dry-day field campaign on August 12th, 2020

Concentrations in surface water

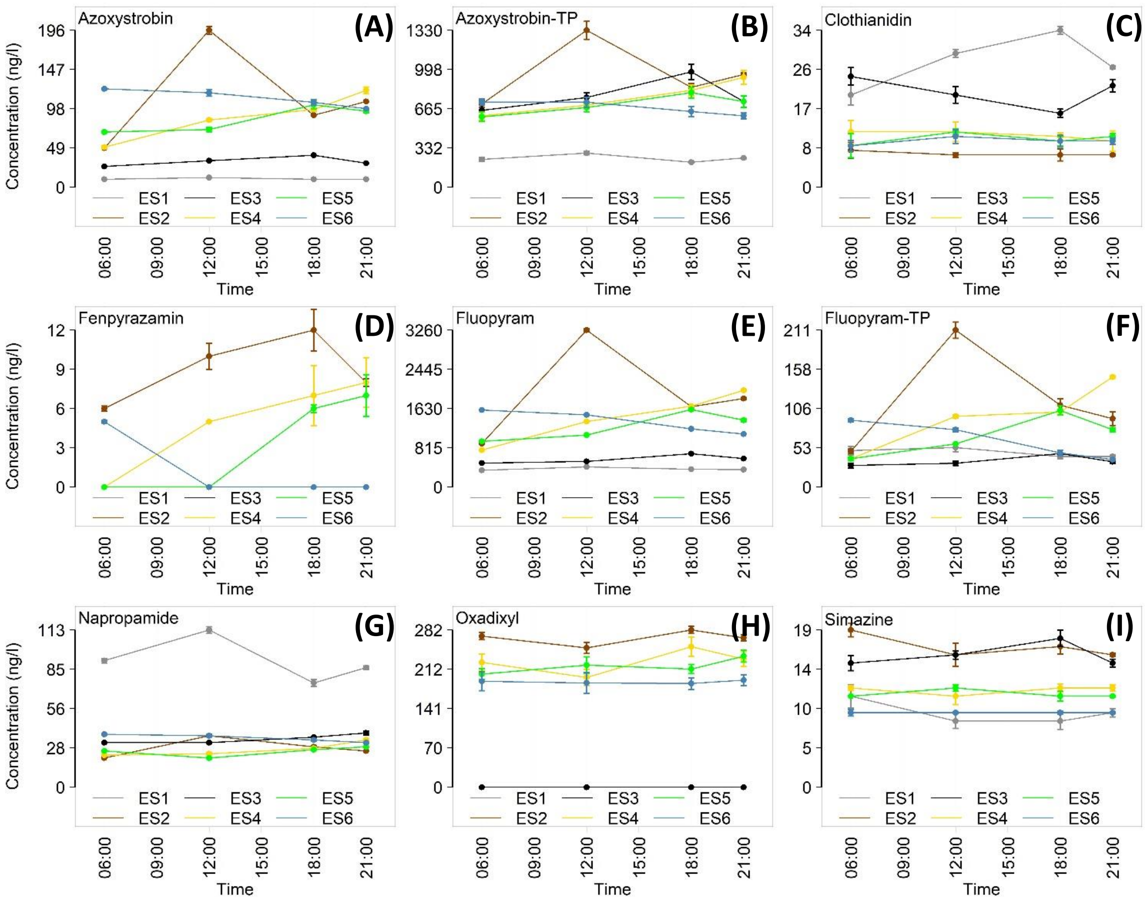

Figure S13: Concentrations in surface water from the dry-day campaign. Data points are grouped by compound, coloured by location and depicted over time. The vertical bars indicated the standard deviation of the measurements (mean concentration of 3 injections of the same sample). Concentration values smaller than LOQ were set to 0 ng/l for visualization purposes. Mesotrione not shown because its concentrations were always below LOQ.

Spatial variability of concentrations in surface water

Because we measured fluctuations in concentrations at the outlet of the catchment in 2019, we aimed to understand the variability in concentrations in two scenarios: along the stream at the same time (Figure S14) and over time at the same location (Figure S15). The variability is defined as an underestimation ratio calculated as the ratio between maximum and minimum concentrations for each compound for the two studied scenarios. The variability along the catchment at a given time (Figure S14) is generally higher than the variability over time at a given location (Figure S15). This points to the presence of influential contamination sources in the catchment. Azoxystrobin showed the largest variability along the catchment at a given time (Figure S14). The variability showed a decreasing trend from the right side of the catchment to the outlet of the catchment (Figure S15).

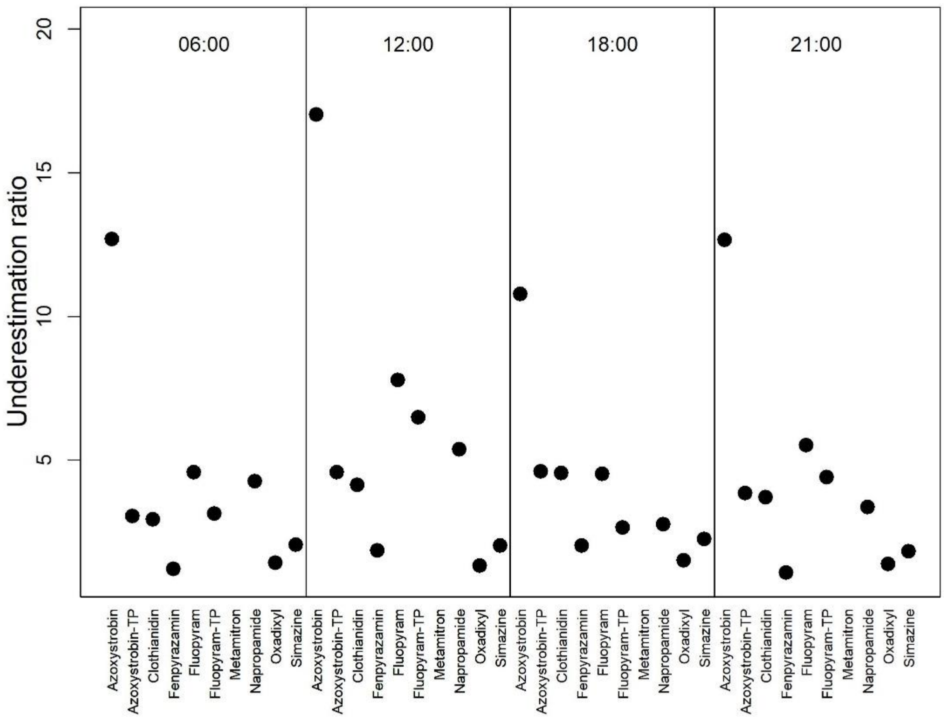

Figure S14: Ratio between maximum and minimum concentrations in surface water, by compound over space at a given time, which is reported in the top of the figure.

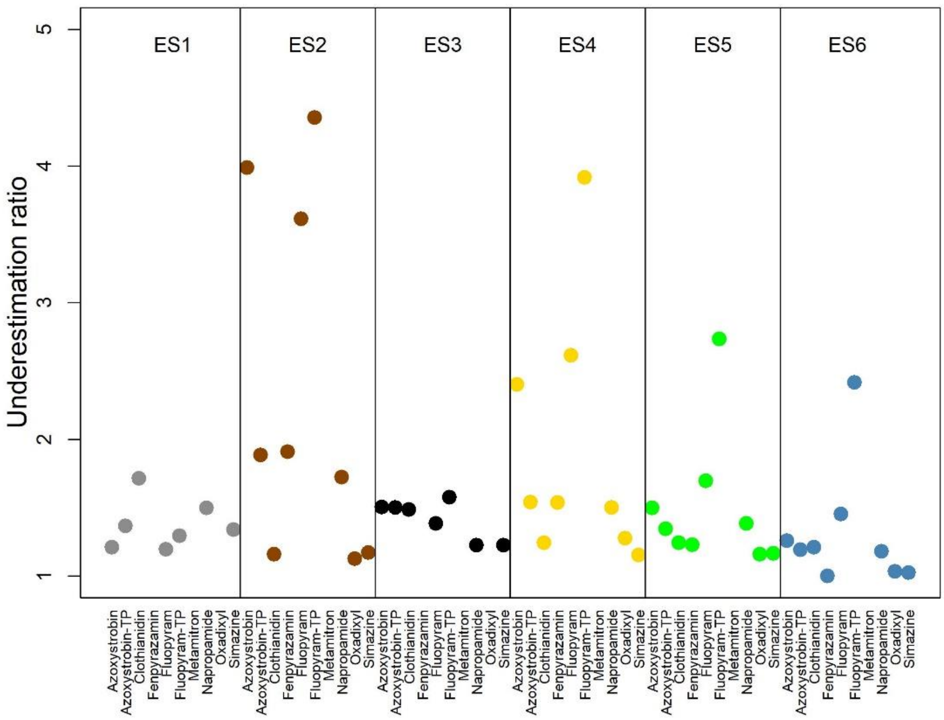

Figure S15: Ratio between maximum and minimum concentrations in surface water, by compound over time at a given location. The colors correspond to the sampled location, which is reported in the top of the figure.

Concentrations in tile drains

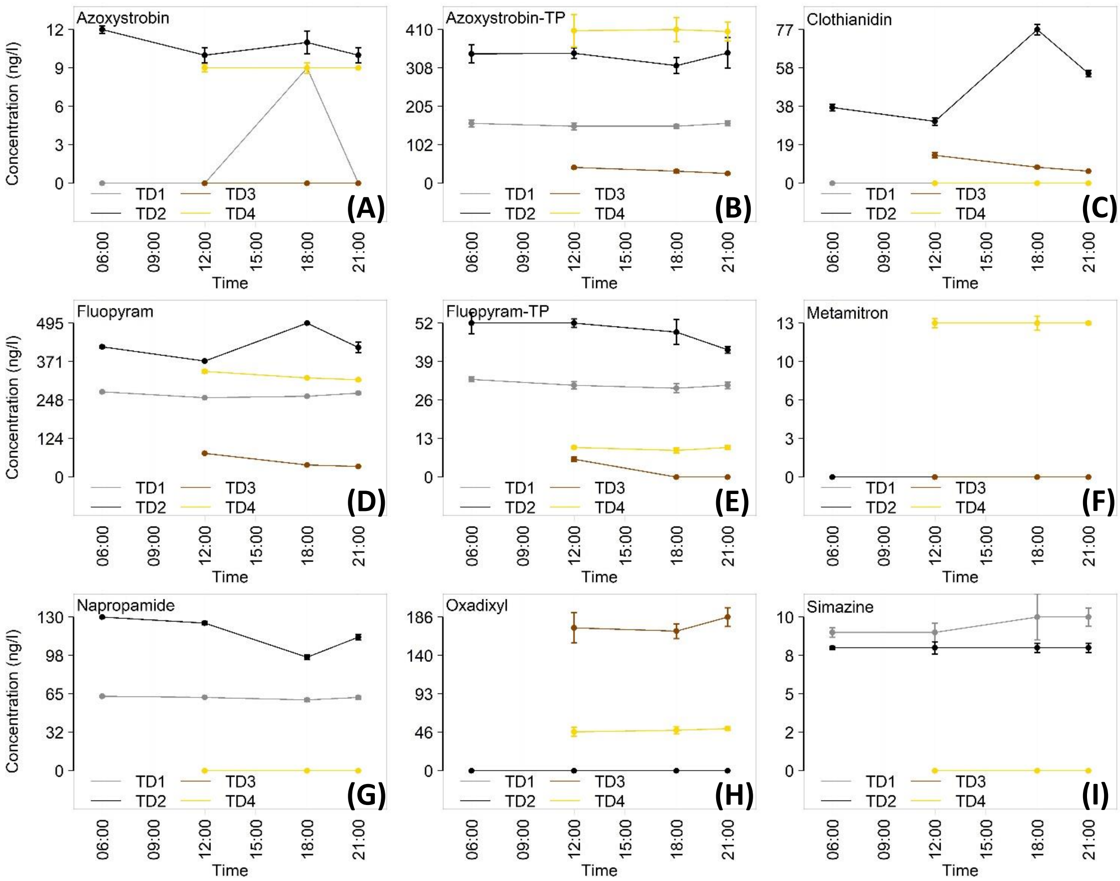

Figure S16: Concentrations in tile drain outlets from the dry-day campaign. Data points are grouped by compound, coloured by location and depicted over time. Fenpyrazamin not shown because its concentrations were below the LOQ. Concentration data for TD3 and TD4 at 06:00 were missing because the precise positions of these outlets were not known and were not found initially. The vertical bars indicated the standard deviation of the measurements (mean concentration of 3 injections of the same sample). Concentration values smaller than LOQ were set to 0 ng/l for visualization purposes.

Bibliography

la Cecilia, D., Dax, A., Ehmann, H., Koster, M., Singer, H., & Stamm, C. (2021). Continuous high-frequency pesticide monitoring to observe the unexpected and the overlooked. *Water Res X, 13*, 100125. doi:10.1016/j.wroa.2021.100125