Supplementary Information A (SI-A) to:

**Pesticide concentrations in agricultural storm drainage inlets of a small Swiss catchment**

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The datasets generated and analysed in this study (e.g. pesticide concentrations, rainfall data, discharge data) can be downloaded from the Eawag Research Data repository (doi: 10.25678/0005X4).
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A1. Methods

A1.1 Field work

A1.1.1 Sampling sites

Figure A1: Sampling site II. The inlet is situated between a rather flat farm track and a wheat field with moderate slope. The field is separated by a buffer strip of approximately 6 m width from the farm track.
Figure A2: Sampling site I2. The inlet is situated between a flat farm track and a flat sugar beet field. The field is separated from the farm track with a buffer strip of approximately 0.5 m width. The inlet itself is located on the buffer strip and therefore lies directly at the border of the field and the farm track.

Figure A3: Sampling site I3. The site is situated between a steep einkorn wheat field and a steep farm track. The inlet is separated from the farm track by a grass buffer of approximately 0.5 m width. The field is separated from the farm track by a buffer strip of approximately 2 m width.
Figure A4: Sampling site I4. The site is located at a flat farm track below a steep corn field (left), and next to a flat potato field (right). The two fields are separated from the farm track by a grass buffer strip of approximately 1 m.

Figure A5: Picture of an inlet in the catchment. For taking the picture, the gridded lid was removed. The outlet pipe visible is the only pipe in the inlet, and drains to the stream. The water in the inlet stagnates at the height of the outlet pipe bottom.
Figure A6: Outside view of sampling site CS.

Figure A7: Inside view of sampling site CS.
A1.1.2 Water-level proportional samplers

In the following, we provide a short description of the water-level proportional samplers used in the storm drainage inlets. A detailed description of the samplers is provided in Schönenberger et al. (2020). The water-level proportional samplers consisted of a glass bottle with a volume of 1L (DURAN Weithalsglasflasche GLS 80), sealed with a screw cap (DURAN GLS80) which had two openings (Figure A9). One of the openings was equipped with a bent metal tube, the other one with a plastic tubing of 2m length (FESTO PUN 6x1-BL) connected to a needle valve (Bronkhorst precision valve, NV-004-HR).

During rain events, surface runoff entering the inlets produces a rise of the water level in the inlets. When the water level was high enough such that the samplers are submerged (this was the case at a water level of 2 cm for inlets with little runoff, and 3 cm for inlets with larger runoff), water starts to flow into the glass bottle (A) through the metal tube (C). In the bottle, the air is compressed and pressed...
out of the bottle through the needle valve (E). Consequently, an equilibrium between the inflowing water volume, the outflowing air volume, and the compression of air and water in the bottle is established. As soon as this equilibrium is established, an increase of water level pressure leads to an increase in the sampling rate, and consequently, the sampling rate is proportional to the water level. The sampling stops either when the water level drops below the water inlet, or when the sampling bottle is full.

Figure A9: Water-level proportional sampler in a stormwater drainage inlet during a rain event. A: Glass bottle, B: Screw cap, C: Metal tube, D: Plastic tubing, E: Needle valve. F: Fixation of the sampler. G: Weir. Adapted from Schönenberger et al. (2020).
A1.1.3 Sampling strategy

Figure A10: Illustration of the event-based sampling strategy. When the water level threshold was exceeded in at least two of the inlets (I1-I4), the automatic samplers at the collector shaft (CS) and the stream (ST) were triggered via the GPRS module to start sampling. Additionally, water level data and the information about the triggering of the samplers were sent to the research institute via the GPRS modules.

Figure A11: Total masses of pesticides applied in the study catchment per day in 2019 (kg). The red lines depict the start and the end of the study period (01.04.2019 and 20.08.2019). Grey bars show the total pesticide mass applied on the respective day. Black bars show the total pesticide mass applied for only those substances that were analysed within this study. Oils used as pesticides (e.g. paraffin oil, rapeseed oil) were excluded from the analysis. E1 to E19 indicate the rain events sampled in this study.
A1.1.4  Field mapping

![Map of surface runoff flow paths during a snowmelt event on 12 March 2018. The mapped contributing areas are minimal contributing areas and may be much larger in reality. They were only mapped for some of the inlets and may differ for other events. Source of background map: Swisstopo (2020).](image)

Figure A 12: Map of surface runoff flow paths during a snowmelt event on 12 March 2018. The mapped contributing areas are minimal contributing areas and may be much larger in reality. They were only mapped for some of the inlets and may differ for other events. Source of background map: Swisstopo (2020).

A1.2  Chemical analysis

In the following, further details on the chemical analysis procedure are given. A table with all substances measured is given below (Table A3).

Field samples were stored at -20° until further process. After thawing, the sample was shaken, and 1.5 ml sample was transferred to a 1.5 ml vial and closed with a magnetic starburst cap. The sample preparation was achieved through a fully automated workflow using a PAL RTC (CTC analytics AG, Switzerland) equipped with a dilutor tool, centrifuge, C-stack, fast wash station and an injection valve. After centrifugation of the samples (5 min at 2000g), 600 µL of supernatant was aspirated by the dilutor. The dilutor needle was washed by aspirating 10 µL of nanopure water at the fast wash station. Afterwards, 10 µL of a standard mix containing 84 isotopic labelled internal standards (ISTD, details Table A3) at a concentration of 0.01 mg/L was added to the dilutor tubing and separated again with 10 µL of nanopure water. Depending on the sample type either an exact volume of standard solution (concentration: 0.06, 0.006 and 0.0006 mg/L) was added and then equalized by an ethanol volume ranging from 0 to 50 µL.
(standards and spiked samples) or just the equalization volume of 50 µL Ethanol was added (samples and blanks). This ensured constant sample constitution and an organic content of ~5%. The entire sample volume of 670 µL was then transferred into an empty vial equipped with a slitted septa and mixed by aspirating and dispensing the dilutor. Sample preparation occurred interlaced with sample acquisition. During one measurement four samples were prepared as described above.

For the measurement, a volume of 100 µL was injected on to the chromatographic system. Chromatographic separation was achieved using a reversed phase column (Atlantis T3, particle size 3µm, 3.0×150 mm, Waters) and a linear water-methanol gradient, both acidified with 0.1% formic acid. The flow rate was 0.3 µL/min and the column temperature was 30°C. The gradient was as follows: 0-1.5 min constant at 0% methanol, 1.5-18.5 min linear gradient to 95% methanol, 18.5-30.5 min constant at 95% methanol followed by equilibration (0% methanol) for 3.5 min. Data acquisition was accomplished with a Lumos Fusion (Thermo Fisher Scientific) running in positive and negative electrospray ionization mode separately (spray voltage: 3500 V in pos, 3000 V in neg). Full scans were recorded with a resolution of 240’000 (at m/z 200) and mass range 100-1000 m/z followed by three data-dependent MS2 scans using higher energy collision-induced dissociation (HCD) at a resolution of 15’000 (at m/z 200).

Peak integration was performed using TraceFinder 5.1 with a mass tolerance of 5 ppm. Substance confirmation occurred through comparison of the retention time, exact mass and fragment spectra with reference material. Quantification was achieved with a linear calibration curve using the peak area ratio of the analyte and ISTD. The calibration curve ranged from 10 to 5000 ng/L. For compounds without structurally identical ISTD, a closely eluting or structurally similar ISTD was chosen to reach the best relative recovery (close to 100% in spiked samples). The assignment of ISTDs and relative recoveries are shown in Table A3. For those compounds, the concentrations were corrected by the relative recovery. The LOQ was determined by the concentration of the lowest standard that was still detected with a good chromatographic peak (at least 4 sticks) and whose area was at least 4 times higher than in laboratory or field blank samples. The lowest calibrations standard value was then corrected by the matrix factor for the final LOQ. For 80% of the compounds, the LOQ was 20 ng/L or lower (see Table A3). For quality control, 54 laboratory and 11 field blanks were measured and taken into account for the LOQ. Additionally, 18 random samples were spiked with 50 and 500 ng/L to determine the relative recovery and matrix suppression.
A1.3 Data analysis

A1.3.1 Surface runoff connectivity model

Table A1: Parameters of the surface runoff connectivity model used for determining catchments of inlets, river, and internal sinks.

| Parameter                  | Value                                                |
|----------------------------|------------------------------------------------------|
| Hedge infiltration        | No hedges in the catchment                          |
| Forest infiltration width  | No infiltration in forests                          |
| Road carving depth         | 25 cm                                                |
| Sink depth                 | 25 cm                                                |
| Shortcut definition        | Only inlets act as shortcut                         |
| Maximal flow distance      | No restriction on maximal flow distance              |

A1.3.2 Discharge measurement in inlets

As mentioned in Sect. 2.4.4, the discharge in the inlets was determined using water level measurements combined with triangular weirs for which a rating curve was calibrated. The weirs consisted of stainless chromium steel plates with two triangles of different slopes cut out (see Figure A13), and were installed in front of the outlet pipes of the measured inlets. The space between the outlet pipe and the weir was sealed with rubber.

For determining the rating curve of the weirs, their wetted area was split into three areas A, B, and C, as shown in Figure A13. For each area, a separate rating curve was determined and the rating curve of the weir was calculated by summing up the contributions of all three areas (eq. A2.1 to A2.3).

Area A was defined as the wetted area for water levels \( p \) smaller or equal to the water level at the slope changing point of the triangular weir \( p_{wc} \). For this area, the weir corresponds to a normal triangular weir and its rating curve can be described according to eq. A1.1 (Aigner 2008). Area B was defined as the wetted area between the slope changing point of the triangular weir \( p_{wc} \) and the water level up to which the discharge was calibrated \( p_{cal,max} \). We neglected the influence of flow in area A on the flow in area B and assumed that the shape of the rating curve of area B corresponded to the curve of a trapezoid weir (eq. A1.2, Aigner 2008).

For area C (water levels higher than \( p_{cal,max} \)), we created three different assumptions, corresponding to a minimum \( Q_{min} \), moderate \( Q_{mod} \) and high \( Q_{high} \) discharge estimate (example, see Figure A14). For the minimum estimate (eq. A2.1), we set the upper discharge limit to the maximal discharge for which the weir was calibrated \( Q(p_{cal,max}) \). For the moderate estimate (eq. A2.2), we assumed the shape of the rating curve in area C to correspond to the curve of a circular weir (eq. A1.3, Aigner 2008). The upper discharge limit was set to the discharge calculated for the water level at the upper weir end \( p_{max} \). For
the high estimate (eq. A2.3), we extrapolated the shape of the rating curve of area B (eq. A1.2) and set an upper discharge limit to the discharge calculated for \( p_{\text{max}} \).

The weir discharge coefficients \( \mu_{\text{tri}} \) and \( \mu_{\text{tra}} \) were calibrated by pouring known discharges into an inlet with a tube and measuring the emerging water levels. Since no discharges corresponding to water levels higher than \( p_{\text{cal,max}} \) could be produced with the tube, the coefficient \( \mu_{\text{cir}} \) was calibrated using only one data point (i.e. the data point at water level \( p_{\text{cal,max}} \)).

\[
Q_{\text{tri}}(p) = \frac{8}{15} \mu_{\text{tri}} \cdot \sqrt{2g} \cdot \frac{b}{2p_{\text{we}}} \cdot p^{\frac{5}{2}} \quad \text{(A1.1)}
\]

\[
Q_{\text{tra}}(p) = \frac{2}{3} \mu_{\text{tra}} \cdot \sqrt{2g} \cdot b \cdot (p - p_{\text{wc}})^{\frac{1}{2}} \left( 1 + \frac{4(p - p_{\text{wc}})w}{b h} \right) \quad \text{(A1.2)}
\]

\[
Q_{\text{cir}}(p) = \mu_{\text{cir}} \cdot \sqrt{2g} \cdot d^{\frac{2}{3}} \cdot \left( (p - p_{\text{cal,max}} + r)^{\frac{11}{6}} - r^{\frac{11}{6}} \right) \quad \text{(A1.3)}
\]

\[
Q_{\text{min}} = \begin{cases} 
Q_{\text{tri}}(p) & |p \leq p_{\text{wc}} \\
Q_{\text{tri}}(p_{\text{wc}}) + Q_{\text{tra}}(p) & |p_{\text{wc}} < p \leq p_{\text{cal,max}} \\
Q_{\text{tri}}(p_{\text{wc}}) + Q_{\text{tra}}(p_{\text{cal,max}}) & |p > p_{\text{cal,max}}
\end{cases} \quad \text{(A2.1)}
\]

\[
Q_{\text{mod}} = \begin{cases} 
Q_{\text{tri}}(p) & |p \leq p_{\text{wc}} \\
Q_{\text{tri}}(p_{\text{wc}}) + Q_{\text{tra}}(p) & |p_{\text{wc}} < p \leq p_{\text{cal,max}} \\
Q_{\text{tri}}(p_{\text{wc}}) + Q_{\text{tra}}(p_{\text{cal,max}}) + Q_{\text{cir}}(\min(p, p_{\text{max}})) & |p > p_{\text{cal,max}}
\end{cases} \quad \text{(A2.2)}
\]

\[
Q_{\text{high}} = \begin{cases} 
Q_{\text{tri}}(p) & |p \leq p_{\text{wc}} \\
Q_{\text{tri}}(p_{\text{wc}}) + Q_{\text{tra}}(p) & |p_{\text{wc}} < p \leq p_{\text{cal,max}} \\
Q_{\text{tri}}(p_{\text{wc}}) + Q_{\text{tra}}(\min(p, p_{\text{max}})) & |p > p_{\text{cal.max}}
\end{cases} \quad \text{(A2.3)}
\]

with:

- \( Q_{\text{tri}}, Q_{\text{tra}}, Q_{\text{cir}} \): Rating curves for the triangular, trapezoid, and circular part of the weir (m³ s⁻¹)
- \( Q_{\text{min}}, Q_{\text{mod}}, Q_{\text{high}} \): Minimal, moderate, and high discharge estimate (m³ s⁻¹)
- \( p \): Water level (m)
- \( p_{\text{wc}} \): Water level at the slope changing point of the triangular weir (= 0.03 m)
- \( p_{\text{cal,max}} \): Maximal water level up to which the weir was calibrated (m)
- \( p_{\text{max}} \): Water level at the upper end of the weir (= 0.075 m)
- \( b, h, w \): Dimensions of the triangular weir (m) (see Figure A13)
- \( d \): Diameter of the outlet pipe (m)
- \( r \): Radius of the outlet pipe (m)
- \( g \): Acceleration due to gravity (= 9.807 m s⁻²)
- \( \mu_{\text{tri}}, \mu_{\text{tra}}, \mu_{\text{cir}} \): Weir discharge coefficients (-)
Figure A13: Dimensions of the triangular weir (grey area) and the subareas used for rating curve determination.

Figure A14: Rating curve of the triangular weir installed in inlet 3. The black solid line represents the moderate discharge estimate ($Q_{\text{mod}}$) and the black dashed lines represent the minimal and high discharge estimates ($Q_{\text{min}}$ and $Q_{\text{high}}$). The red dots show the measurements used for calibration of the rating curve.
To compare the discharge in the inlets and the stream, we calculated the ratio between the discharge sum of all four inlets to the discharge in the stream ($r_Q$) (eq. A3.1). For the discharge measured in the stream $Q_{\text{stream}}$, the cantonal authorities provided no information on uncertainty. Expecting that the relative uncertainty of the discharge through inlets is much larger than the uncertainty in stream discharge, we neglected the latter.

$$r_Q = \left( \frac{r_{Q,\text{min}}}{r_{Q,\text{mod}}} \right) = \frac{\sum_{i=1}^{4} Q_{\text{inl},i}}{Q_{\text{stream}}}$$

(A3.1)

$Q_{\text{inl},i}$: Discharge estimates (minimum, moderate, high) in inlet i (m$^3$ s$^{-1}$)

$Q_{\text{stream}}$: Discharge in the stream (m$^3$ s$^{-1}$)

Additionally, we calculated the ratio between the discharge sum in inlets and the fast discharge in the stream ($r_{Q,\text{fast}}$) (eq. A3.2).

$$r_{Q,\text{fast}} = \left( \frac{r_{Q,\text{fast},\text{min}}}{r_{Q,\text{fast},\text{mod}}} \right) = \frac{\sum_{i=1}^{4} Q_{\text{inl},i}}{Q_{\text{stream},\text{fast}}}$$

(A3.2)

$Q_{\text{stream},\text{fast}}$: Fast discharge fraction estimates in the stream (m$^3$ s$^{-1}$)

We estimated the fast discharge fraction in the stream using a recursive filter technique (Lyne and Hollick, 1979) for discharge separation (function “BaseflowSeparation” of the R package “EcoHydRology”, version 0.4.12.1, Fuka et al. (2018)). We used three different filter parameters (0.9, 0.925, and 0.95; see Nathan and McMahon (1990)) to come up with a low, moderate, and high estimate of the fast discharge fraction.

Based on the discharge measurements in the four inlets, we estimated the total discharge flowing through all inlets in the catchment $Q_{\text{inl,tot}}$. For this, we used three simple extrapolation methods. In the first two methods, we assumed that the discharge in an inlet is proportional to the road area (eq. A4.1) or to the agricultural area connected to the inlet (eq. A4.2). In the third method, we assumed that the discharge is proportional to the number of inlets (eq. A4.3). These three methods are meant to provide a rough estimate of the total discharge and various parameters influencing the total discharge (such as slope, soil permeability, crop types, spatial distribution of rainfall) were not taken into account here.

$$Q_{\text{inl,tot,road}} = \frac{\sum_{i=1}^{4} A_{\text{road},i}}{A_{\text{road,tot}}} \cdot \sum_{i=1}^{4} Q_{\text{inl},i}$$

(A4.1)

$A_{\text{road},i}$: Road area connected to inlet i (m$^2$)

$A_{\text{road,tot}}$: Total road area connected to inlets in the catchment (m$^2$)

$Q_{\text{inl},i}$: Discharge in inlet i (m$^3$ s$^{-1}$)
\[ Q_{\text{inl, tot, agri}} = \frac{\sum_{i=1}^{4} A_{\text{agri, } i}}{A_{\text{agri, tot}}} \cdot \sum_{i=1}^{4} Q_{\text{inl, } i} \]  

(A4.2)

\[ A_{\text{agri, } i}: \text{Agricultural area connected to inlet } i \left( m^2 \right) \]

\[ A_{\text{agri, tot}}: \text{Total agricultural area connected to inlets in the catchment} \left( m^2 \right) \]

\[ Q_{\text{inl, tot, num}} = \frac{n_{\text{inl, tot}}}{n_{\text{inl, measured}}} \cdot \sum_{i=1}^{4} Q_{\text{inl, } i} = \frac{158}{4} \cdot \sum_{i=1}^{4} Q_{\text{inl, } i} \]  

(A4.3)

\[ n_{\text{inl, measured}}: \text{Number of inlets with discharge measurements (--) \}} \]

\[ n_{\text{inl, tot}}: \text{Total number of inlets in the catchment (--) \}} \]

### A1.3.3 Model of concentrations in inlets

Table A2: Overview over the variables used for building the linear mixed model.

| Variable                              | Abbreviation | Type         | Discrete/ Continuous | Unit       | Range/Categories |
|---------------------------------------|--------------|--------------|----------------------|------------|-----------------|
| Inlet concentration                   | log10(c)     | Response variable | Continuous            | ng L\(^{-1}\) | log10([5, 62000]) |
| Time since application                | t\(_{\text{appl}}\) | Fixed effect | Continuous            | days       | [1.2, 142]      |
| Amount of pesticide applied per area  | log10(m\(_{\text{appl}}\)) | Fixed effect | Discrete              | g ha\(^{-1}\) | log10([1.2, 1600]) |
| Freundlich adsorption coefficient     | log10(K\(_{\text{foc}}\)) | Fixed effect | Discrete              | mg L\(^{-1}\) | log10([20, 4900]) |
| normalized to organic carbon content  |                           |              |                      |            |                 |
| Octanol-water partition coefficient   | log10(K\(_{\text{ow}}\)) | Fixed effect | Discrete              | -          | [-1.2, 4.7]     |
| Half-life in water                    | DT\(_{50, \text{water}}\) | Fixed effect | Discrete              | days       | [0.30, 92]      |
| Half-life in soil                     | DT\(_{50, \text{soil}}\) | Fixed effect | Discrete              | days       | [0.34, 500]     |
| Moderate estimate of the discharge in | log10(Q\(_{\text{mod}}\)) | Fixed effect | Continuous            | L          | log10([0, 8500]) |
| the event                             |                           |              |                      |            |                 |
| Potential transport processes involved | p\(_{\text{transport}}\) | Fixed effect | Categorical           | -          | (A, B, C, D)    |
|                                       |                           |              |                      |            | (see Sect. 2.4.3) |
| Inlet sampled                         | i                         | Random effect | Categorical           | -          | (1, 2, 3, 4)    |
Table A3: List of the 51 substances analysed. P: Pesticide, TP: Transformation product, LOQ: Limit of quantification, RR: Relative recovery, LMM: Substance used in the linear mixed model. The samples were measured in three sets. Below, we therefore report the LOQs and RRs for each set.

| Substance measured | CAS number | InChIKey | Substance type | Pesticide class | LOQ Set 1 (ng/L) | LOQ Set 2 (ng/L) | LOQ Set 3 (ng/L) | RR set 1 (%) | RR set 2 (%) | RR set 3 (%) | Semi-quantitative | Internal standard | LM M |
|--------------------|------------|----------|----------------|-----------------|-----------------|-----------------|-----------------|--------------|--------------|--------------|-------------------|-----------------|------|
| Azoxylostrobin     | 131860-33-8| WFDX0XNFRHIEA-N | P              | Fungicide       | 7               | 9               | 6               | 78           | 82           | 97           | no                | Azoxylostrobin D4 |      |
| Bixafen            | 581809-46-3| LDMO0XUCMHBZ-UHFFFAOYSA-N | P              | Fungicide       | 8               | 20              | 5               | 80           | 98           | 105          | no                | Flufenacet D5    | x    |
| Bosalid            | 188425-85-6| WYEMLYFIZORAB-UHFFFAOYSA-N | P              | Fungicide       | 10              | 10              | 4               | 89           | 92           | 93           | no                | Bosalid D4       |      |
| Carfentrazone-ethyl| 128639-02-1| MLKCGVHJBCRD-UHFFFAOYSA-N | P              | Herbicide       | 10              | 20              | 15              | 50           | 83           | 74           | no                | Epoxiconazole D4 | x    |
| Chlortoluron       | 15545-48-9 | DGGMFYXOMFQAI-UHFFFAOYSA-N | P              | Herbicide       | 10              | 6               | 6               | 83           | 97           | 101          | no                | Chlortoluron D6  |      |
| Cymoxanil          | 57966-95-7 | XERJKGBRTKEO-VZUCSMOQA-N | P              | Fungicide       | 9               | 9               | 9               | 76           | 87           | 174          | partially         | Metamitron D5    | x    |
| Cyproconazole      | 94361-06-5 | UFNOUKBIZYDE-UHFFFAOYSA-N | P              | Fungicide       | 8               | 8               | 4               | 83           | 100          | 102          | no                | Dimethenamid D3  |      |
| Difenoconazole     | 119446-68-3| BOYATMOXGDBH-UHFFFAOYSA-N | P              | Herbicide       | 25              | 8               | 8               | 121          | 106          | 114          | no                | Pyraclostrobin D3 | x    |
| Disiflucanil       | 83164-33-4 | WYEFWKOIOXV-JD-UHFFFAOYSA-N | P              | Herbicide       | 500             | 200             | 100             | 81           | 143          | 103          | no                | Metafenone D9    |      |
| Dimethachlor       | 50563-36-5 | SCCDNNKJYDZMM-UHFFFAOYSA-N | P              | Herbicide       | 6               | 9               | 10              | 79           | 86           | 106          | partially         | Dimethenamid D3  |      |
| Dimethenamid       | 87674-68-8 | ILYFTQDENKRO-UHFFFAOYSA-N | P              | Herbicide       | 9               | 8               | 4               | 89           | 102          | 98           | no                | Dimethenamid D3  | x    |
| Epoxiconazole      | 13385-98-8 | ZMYFCFLBAQGRS-UHFFFAOYSA-N | P              | Fungicide       | 7               | 8               | 6               | 75           | 78           | 99           | no                | Epoxiconazol D4  | x    |
| Ethofumesate       | 26225-79-6 | IRCMYGHIKLGW-UHFFFAOYSA-N | P              | Herbicide       | 9               | 20              | 10              | 88           | 109          | 87           | no                | Azoxystrobin D4  | x    |
| Fenpropimorph      | 67306-03-0 | RYASSKMOXZMBAI-ALOPSCKC-N | P              | Herbicide       | 6               | 5               | 10              | 64           | 105          | 93           | no                | Metribuzin D3    | x    |
| Florasulan         | 145701-23-1| QZAXATCPQKOEI-UHFFFAOYSA-N | P              | Herbicide       | 100             | 50              | 20              | 73           | 91           | 95           | no                | 2,4-D3            | x    |
| Fluazifop (free acid) | 69335-91-7| YUUKUEAFVLDW-UHFFFAOYSA-N | P              | Herbicide       | 40              | 9               | 10              | 100          | 103          | 98           | no                | Mecoprop D6      |      |
| Fluazinam          | 79622-59-6 | UZGCWKLCPDCTF-UHFFFAOYSA-N | P              | Fungicide       | 200             | 8               | 4               | 345          | 123          | 121          | no                | Fipronil 13C15N2 |      |
| Flufenacet         | 142459-58-3| TANUCZTCDJ-UHFFFAOYSA-N | P              | Herbicide       | 8               | 20              | 6               | 84           | 98           | 91           | no                | Flufenacet D4    |      |
| Fluopicolide       | 239110-15-7| GBOYJIYACLON-UHFFFAOYSA-N | P              | Fungicide       | 8               | 9               | 2               | 97           | 99           | 109          | no                | Dimethenamid D3  |      |
| Herbicide | Fungicide | Fungicide | Herbicide | Herbicide | Herbicide | Herbicide | Fungicide | Herbicide |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Flupyradolu-methyl | 14470-53-4 | DTVOKYXYXYACGTVG | O-UHFFFAOYA-N | P | Herbicide | 10 | 9 | 10 | 66 | 105 | 102 | no | Boscalid D4 |
| Foramsulforon | 173159-57-4 | PXDNJSDQBOBLS-UHFFFAOYA-N | P | Herbicide | 9 | 9 | 4 | 80 | 93 | 97 | partially | Metribuzin D3 |
| Iodosulfuron-methyl | 185119-76-0 | VWGAYSCWLXOH0Q-UHFFFAOYA-N | P | Herbicide | 10 | 15 | 10 | 47 | 102 | 100 | no | Azoxystrobin D4 | x |
| Isoproturon | 34123-59-6 | PUYMSZJZQOOZ-UHFFFAOYA-N | P | Herbicide | 2 | 4 | 6 | 82 | 94 | 103 | partially | Isoproturon D5 |
| Lenacil | 2164-08-1 | ZTMKADLOYKWC-A-UHFFFAOYA-N | P | Herbicide | 10 | 15 | 8 | 88 | 100 | 100 | no | Lenacil(cyclohexyl) D4 | x |
| Mandipropamid | 37472-66-2 | KWLWJPIJKMCM-UHFFFAOYA-N | P | Fungicide | 8 | 9 | 4 | 92 | 108 | 117 | no | Dimethenamid D3 |
| Mecoprop | 93-65-2 | WNTGYJOUMFZEP-UHFFFAOYA-N | P | Herbicide | 100 | 40 | 5 | 84 | 109 | 95 | no | Mecoprop D6 | x |
| Mesosulfuron-methyl | 74223-64-6 | RSMUVRYMZCOLB-H-UHFFFAOYA-N | P | Herbicide | 8 | 8 | 9 | 89 | 99 | 120 | no | Dimethenamid D3 | x |
| Metamitron | 41394-05-2 | VHCNQEUWZYOAE-V-UHFFFAOYA-N | P | Herbicide | 20 | 7 | 8 | 89 | 105 | 109 | no | Metamitron D5 | x |
| Metolachlor | 51218-45-2 | WVQBLGZPHQPPF-UHFFFAOYA-N | P | Herbicide | 8 | 8 | 4 | 91 | 85 | 95 | no | Metolachlor D6 |
| Metrafenone | 220899-03-6 | AMSPWYOQAAWRR-M-UHFFFAOYA-N | P | Fungicide | 15 | 9 | 6 | 83 | 95 | 93 | no | Metrafenone D9 | x |
| Metribuzin | 21087-64-9 | FOXFXKUHHCZPX-UHFFFAOYA-N | P | Herbicide | 9 | 7 | 4 | 84 | 95 | 99 | no | Metribuzin(S-methyl-D3) | x |
| Napropamide | 15299-99-7 | WXZVAROIGSFCL-F_UHFFFAOYA-N | P | Herbicide | 8 | 10 | 6 | 71 | 88 | 103 | no | Terbutylazin D5 |
| Nicosulfuron | 111991-09-4 | RTCOGUMHFFWOWJ-UHFFFAOYA-N | P | Herbicide | 10 | 8 | 6 | 92 | 98 | 92 | no | Nicosulfuron D6 |
| Pencycuron | 66063-05-6 | OGYFATSSENKRG-UHFFFAOYA-N | P | Seed treatment | 15 | 9 | 6 | 96 | 91 | 105 | no | Metolachlor D6 | x |
| Propamocarb | 24579-73-5 | WZLZDXDQQPOKN-W-UHFFFAOYA-N | P | Fungicide | 5 | 25 | 50 | 139 | 135 | 110 | no | Metribuzin(S-methyl-D3) |
| Propiconazole | 60207-90-1 | STIIVLHWMQZPCR-UHFFFAOYA-N | P | Fungicide | 15 | 8 | 6 | 104 | 106 | 106 | no | Metrafenone D9 | x |
| Prosulfocarb | 52888-80-9 | NQLVQOSINXZLKG-UHFFFAOYA-N | P | Herbicide | 15 | 8 | 2 | 104 | 86 | 88 | no | Epoxiconazol D4 | x |
| Pyrothioconazole | 178928-70-6 | MNNVNNIOQKVDH-UHFFFAOYA-N | P | Fungicide | 100 | 200 | 100 | 50 | 74 | 81 | no | Pyraclostrobin D3 |
| Pyraclostrobin | 175013-18-0 | HZRSNVLVRUWDEFX-UHFFFAOYA-N | P | Fungicide | 50 | 9 | 15 | 81 | 101 | 96 | no | Pyraclostrobin D3 |
| Spiroxamine | 118134-30-8 | UYOXTUJRZLUCW-UHFFFAOYA-N | P | Fungicide | 100 | 25 | 20 | 153 | 144 | 61 | no | Nicosulfuron D6 |
| Tembotrione | 335104-84-2 | LQAXCUIEPEPSF-UHFFFAOYA-N | P | Herbicide | 50 | 8 | 8 | 62 | 111 | 109 | no | Azoxystrobin D4 |
| Terbuthylazine | 5915-41-3 | FZXISNSWETYPMF-UHFFFAOYA-N | P | Herbicide | 9 | 7 | 6 | 85 | 100 | 101 | no | Terbutylazin D5 | x |
| Product | CAS Number | Description | Contact | Rate | Primary Active Ingredient | Secondary Active Ingredient |
|---------|------------|-------------|---------|------|--------------------------|----------------------------|
| Thiacloprid | 111988-49-9 | Insecticide | P | 4 | Thiacloprid | HOKKPVIRMVDYPB-UHFFAOYSA-N |
| Thiamethoxam | 153719-23-4 | Insecticide | P | 4 | Thiamethoxam | NWWZPOKUIAIW-DHIZIOJOSA-N |
| Trifloxystrobin | 141517-21-7 | Insecticide | P | 4 | Trifloxystrobin | ONCZWDURRAWTVF-TVJDWFNSA-N |
| CT-TP-R417888 | | Fungicide TP | TP | 4 | Metrafenone D9 | x |
| CT-TP-R471811 | | Fungicide TP | TP | 4 | 2,4-D3 | no |
| CT-TP-R611968 | | Fungicide TP | TP | 4 | 2,4-D3 | no |
| CT-TP-SYN507900 | | Fungicide TP | TP | 4 | Fipronil 13C15N2 | no |
| Metamitron-desamino | 36993-94-9 | Herbicide TP | TP | 4 | Metamitron D5 | no |
| Metolachlor-OXA | 152019-73-3 | Herbicide TP | TP | 4 | Metolachlor D6 | no |
A2. Results

A2.1 Hydrological behaviour of inlets

Table A4: Event rainfall needed at different inlets for surface runoff to enter the inlet. The duration of the corresponding rain events equalled 1 to 41 hours (median: 9 hours).

| Location                      | I1  | I2  | I3  | I4  |
|-------------------------------|-----|-----|-----|-----|
| Minimal amount of rainfall leading to discharge (mm) | 1.3 | 1.5 | 3.6 | 1.3 |
| Minimal rainfall always leading to discharge (mm)      | 3.5 | 11.5| 18.8| 3.5 |

Figure A15: Distribution of the total event discharge ratio between each single inlet and the sum of all four inlets.
Figure A16: Number of events exceeding a given event discharge in inlets. Isum corresponds to the discharge sum of all four inlets. Bold lines indicate the moderate discharge estimate \( Q_{i,e,\text{mod}} \). Thin lines indicate the minimum \( Q_{i,e,\text{min}} \) and high discharge estimates \( Q_{i,e,\text{high}} \).

Table A5: Fractions of fast and total discharge in the stream originating from inlets for events with total rainfall > 10 mm. Numbers report the moderate estimates. In brackets, the minimum and high estimates are given. The first column shows the measured discharge fractions in the four studied inlets, the second to fourth column show the extrapolation to all inlets in the catchment according to three different methods (i.e. proportional to the road area, the agricultural area, and the number of inlets; see eq. A4.1 to A4.3).

| Fraction of fast discharge \( r_{Q,\text{fast}} \) | Measured inlets (I1-I4) | Extrapolation to all inlets |
|---------------------------------|---------------------------|-----------------------------|
|                                 | Road area                 | Agri. area                  | Number of inlets |
| 0.83% [0.64%; 1.1%]            | 29% [22%; 38%]            | 14% [11%; 19%]              | 33% [25%; 43%] |
| 0.22% [0.21%; 0.25%]           | 7.5% [7.2%; 8.8%]         | 3.7% [3.6%; 4.4%]           | 8.5% [8.2%; 10%] |
Figure A17: Ratio between total discharge originating from the four inlets and the discharge in the stream $r_Q$. Points indicate the moderate estimate ($r_{Q,\text{mod}}$) and the error bars correspond to the minimum and high estimate ($r_{Q,\text{min}}$ and $r_{Q,\text{high}}$). Sampling event numbers are indicated with white boxes. The black line represents a smoothed conditional mean (LOESS) of the average $r_Q$ estimates, obtained by a locally weighted scatterplot smoothing (LOESS) using the R package ggplot2 (version 3.3.3, function `geom_smooth`). The grey area represents the corresponding 95% confidence interval.
## A2.2 Concentrations and loads

Table A6: Overview over events analysed. II-I4: Inlets 1 to 4, CS: collector shaft, ST: stream. The column “top ten events” shows the top ten events with respect to sum concentrations in the inlets. The letter A indicates that for the respective event samples in the collector shaft and in the stream were analysed. The letter N indicates that for the respective event only samples in the inlets were analysed. In the column “samples analysed” the sample types are indicated: c: water-level proportional composite sample, g: grab sample after the event, t: time proportional sample, b: time proportional backup sample of cantonal authorities, -: no sample available. Sampling interval: The first number indicates the sampling interval of time proportional samples in the collector shaft that were then pooled together into one composite sample with a total sampling time as indicated in brackets.

| Event ID | Starting time | Sum concentrations in I1 to I4 (ng/L) | Discharge sum (L) | Top ten events | Samples analysed | Sampling interval CS (min) |
|----------|---------------|---------------------------------------|-------------------|----------------|------------------|---------------------------|
|          |               | I1 I2 I3 I4 ST                        |                   |                |                  |                           |
| 1        | 03.04 13:57   | 832 8519 162 122 1.4e5                | 33.9 0.9 6.0      | 1.7e4          | c c c c          |                           |
| 2        | 26.04 01:57   | 38 597 0 4 2.8e5                      | 5.3 0.8 3.6       | 7.1e3          | c g -             |                           |
| 3        | 27.04 21:42   | 387 1472 68 99 1.1e5                 | 11.5 0.3 10.8     | 1.3e4          | c c c c          |                           |
| 4        | 04.05 16:32   | 555 1329 0 4 5.4e5                   | 8.6 0.5 3.6       | 5.9e3          | c c -             |                           |
| 5        | 08.05 13:37   | 1820 7355 327 1018 2.0e6             | 22.2 1.3 6.0      | 4.4e4          | A c c c c t t t t |                           |
| 6        | 20.05 00:42   | 2306 1111 3586 1406 2.7e6            | 31.1 1.4 6.0      | 2.9e4          | A c c c c - t t t |                           |
| 7        | 25.05 17:02   | 139 1 0 2 4.4e5                      | 4.6 0.5 6.0       | 3.6e4          | N c g g g         |                           |
| 8        | 28.05 07:17   | 814 379 439 165 8.8e5                | 11.7 1.1 8.4      | 1.7e4          | N c c -           |                           |
| 9        | 29.05 17:57   | 865 960 136 606 4.3e5                | 4.7 1.3 25.2      | 1.9e4          | N c c g c         |                           |
| 10       | 06.06 10:12   | 437 5 0 5 9.7e5                      | 7.3 0.9 4.8       | 1.9e4          | A g g g g t b     |                           |
| 11       | 10.06 11:52   | 5378 7034 951 1721 8.7e6             | 38.2 0.9 9.6      | 2.8e4          | N c c c c         |                           |
| 12       | 15.06 17:57   | 5230 3379 586 4109 3.5e6             | 21.5 8.6 58.8     | 8.9e4          | A c c g c t t t t |                           |
| 13       | 01.07 18:07   | 988 249 0 30 7.7e5                   | 11.6 1.8 27.6     | 6.5e4          | A c c g t b t b   |                           |
| 14       | 06.07 09:42   | 642 98 0 9 9.7e5                      | 8.9 1.8 10.8      | 8.7e4          | A g g g g - b     |                           |
| 15       | 14.07 21:47   | 1185 1547 33 111 7.0e5               | 15.1 2.0 8.4      | 2.3e4          | N c c g g         |                           |
| 16       | 28.07 12:17   | 427 94 0 12 2.8e5                    | 14.5 0.8 10.8     | 1.7e4          | g g g g           |                           |
| 17       | 06.08 07:07   | 865 531 0 117 4.9e5                   | 16.7 1.1 24.0     | 1.6e4          | e c g g           |                           |
| 18       | 10.08 03:42   | 2087 2349 144 614 1.6e6               | 25.4 2.0 58.8     | 1.3e4          | c c c c           |                           |
| 19       | 18.08 22:32   | 1311 1099 28 224 8.6e5                | 18.8 2.0 50.4     | 1.2e4          | g g g g           |                           |
Table A7: Overview over the transformation product concentrations measured at the different sampling sites. To calculate mean concentrations, we replaced concentrations below the limit of quantification (LOQ) by zero (lower value reported) and by the LOQ (higher value reported). The transformation product pattern shown here is most likely caused by the low number of transformation products analysed and does not allow for a general conclusion on transport processes involved. II-I4: inlets, CS: collector shaft, ST: stream.

| Site                        | I1       | I2       | I3       | I4       | CS        | ST        |
|-----------------------------|----------|----------|----------|----------|-----------|-----------|
| Mean transformation product concentration (ng L⁻¹) | 271-301  | 25-56    | 36-66    | 10-43    | 714-716   | 1003-1006 |
| Maximal transformation product concentration (ng L⁻¹) | 7300     | 870      | 550      | 180      | 5200      | 5500      |
| Transformation product with highest concentration | Meta-mitron-Desamino | CT-TP-R471811 | CT-TP-R471811 | Meta-mitron-Desamino | Meta-mitron-Desamino | CT-TP-R471811 |

Figure A18: Concentrations c (ng/L) measured in inlets for event 1 (3 April 2019) to 19 (18 August 2019) for all substances that were found in inlets. White rows indicate that no sample was taken. In the first column, the sample type is indicated. In the remaining columns, substances are clustered by the concentrations measured. coloured dots indicate that the particular substance was applied in the period between the respective and the previous event. Dot colours specify the potential transport processes. LOQ: Limit of quantification.
Figure A19: Concentrations c (ng/L) measured in the collector shaft (event 5, 10, 12, and 13) and in the stream (events 5, 6, 10, 12, 13, 14) for all substances found at one of these two sampling sites. Measurements of events 10, 13, and 14 in the stream originate from backup samples of the cantonal authorities. LOQ: Limit of quantification.

Figure A20: Discharge and terbuthylazine concentration in the stream during event 12 (07.08.2019 to 08.08.2019).
Figure A21: Concentrations of epoxiconazole in inlet 1, during the sampled events (E1 to E19).

Figure A22: Concentrations of pencycuron in inlet 4, during the sampled events (E1 to E19). During E2, E4, and E8, no samples were taken. No pencycuron was found in the first sample (i.e. the concentration was smaller than the limit of quantification (LOQ) of 15 ng/L).
Figure A23: Distribution of pesticide and transformation product concentrations for all sampling sites. Concentrations are assigned to possible responsible transport processes. For substances below the limit of quantification (LOQ), the LOQ was used for the analysis.
Table A8: Result of the linear mixed model. Estimates, t values, and p values are given for each explanatory variable. An explanation of the column “estimates” is provided in the following. For the calculation of p-values, a Kenward-Roger approximation was used for calculating the degrees of freedom. The proportion of variance explained by the fixed factors alone (marginal R^2) was 0.25. The proportion explained by the fixed and random factors (conditional R^2) equalled 0.48.

| Explanatory variable | Abbreviation | Unit | Estimates: Mean [confidence interval: 2.5% – 97.5%] | t value | p value |
|----------------------|--------------|------|-------------------------------------------------|---------|---------|
| Intercept            | Int.         | -    | + (1.4 [ 1.0 – 1.9])                             | 6.24    | < 0.001 |
| Time since application | t_appl     | days | – (2.4 [ 3.9 – 1.0]) \cdot 10^{-3}              | -3.35   | 0.001   |
| Amount of pesticide applied per area (log10) | log_{10}(m_{appl}) | g ha^{-1} | + (2.2 [ 1.5 – 2.9]) \cdot 10^{-1} | 6.24 | < 0.001 |
| Freundlich adsorption coefficient normalized to organic carbon content (log10) | log_{10}(K_{foc}) | mg L^{-1} | – (2.2 [ 3.2 – 1.2]) \cdot 10^{-1} | -4.39 | < 0.001 |
| Half-life in water | DT_{30, water} | days | + (3.2 [ 1.1 – 5.3]) \cdot 10^{-3} | 2.98 | 0.003 |
| Half-life in soil | DT_{30, soil} | days | + (1.1 [ 0.6 – 1.6]) \cdot 10^{-3} | 4.56 | < 0.001 |
| Moderate estimate of the discharge in the inlet during the event (log10) | log_{10}(Q_{mod}) | L | + (1.1 [-4.0 – 6.0]) \cdot 10^{-2} | 0.45 | 0.654 |
| Potential transport processes involved | p_{transport} | - | – (5.1 [ 6.3 – 4.0]) \cdot 10^{-1} | -8.54 | < 0.001 |

To improve the understandability of Table A8, the meaning of the “estimates” column is explained in the following. This column represents the mean estimates of the fixed effects of the linear mixed model and their confidence interval (2.5% to 97.5%). These effects corresponds to an intercept for row 1, to a slope for rows 2 to 7, and to a categorical variable effect for row 8.

In the following, the meaning of these estimates is explained on the example of the variable “time since application” (row 2). In a mathematical notation, our mixed model can be written as follows:

\[
\log_{10}(c) = \text{Intercept} + m_1 \cdot t_{\text{appl}} + m_2 \cdot \log_{10}(m_{\text{appl}}) + m_3 \cdot \log_{10}(K_{\text{foc}}) + \ldots
\]  

(A5)

Where \(m_1, m_2, m_3, \ldots\) are the estimated slopes, \(c\) is the pesticide concentration (ng/L) and \(t_{\text{appl}}\) is the time since application (days). As shown in Table A8, the mean estimate of the slope \(m_1\) equals \(-2.4 \cdot 10^{-3}\) day^{-1}. This means, that the logarithm (log_{10}) of the measured concentration (ng/L) is expected to decrease on average by a factor of \(-2.4 \cdot 10^{-3}\) per day after application.

Table A9: Ratio between pesticide loads in inlets and the stream (moderate estimates, eq. A3.1 and A3.2). In square brackets, the minimum and high estimates are given. Columns show the ratios measured for the sampled inlets, and the ratios resulting from extrapolating the measurements to the entire catchment using three different methods, i.e. proportional to the road area, the agricultural area, and the number of inlets.

| Sampled inlets (11-14) | Extrapolation to entire catchment |
|------------------------|---------------------------------|
|                        | Road area | Agr. area | Number of inlets |
| Mean of single substance load ratios \(r_{\text{L,subst}}\) | 1.8% \[0.77%; 3.7%\] | 61% \[27%; 126%\] | 30% \[13%; 64%\] | 70% \[30%; 144%\] |
| Ratio of load sums \(r_{\text{L,sum}}\) | 0.29% \[0.24%; 0.52%\] | 10% \[8.5%; 18%\] | 5.1% \[4.2%; 9.1%\] | 12% \[9.7%; 21%\] |
Figure A24: Relative loads per inlet compared to the loads transported through the four measured inlets. Left: Pesticides, right: transformation products. The transformation product pattern shown here is most likely caused by the low number of transformation products analysed and does not allow for general conclusions on the transport processes involved.

Figure A25: Sum of loads in the four inlets per substance and event. Only loads > 0 ng are shown.
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