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# Continuous high-frequency pesticide monitoring in a small tile-drained agricultural stream to reveal diel concentration fluctuations in dry periods

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Plant Protection Products (PPPs) pose a threat to surface water quality worldwide. While small streams compose the majority of the stream lengths and are crucial for biodiversity, their exposure patterns to PPPs and transformation products (TPs) are largely understudied in dry periods. This knowledge gap can lead to ineffective monitoring strategies for addressing water quality issues. Here, we focus on two extended dry periods the in-depth analysis of a unique continuous high-frequency (20 min) concentrations dataset for 60 PPPs and TPs. The dataset refers to the monitoring of a small tile-drained agricultural stream over 41 days from May to July in 2019. The overall 2560 concentration data per compound obtained with the on-site mass spectrometer *MS<sup>2</sup>Field* platform revealed: (i) surprisingly high maximum concentrations (hundreds to thousands ng/l for some compounds) over extended periods of time, (ii) novel diel fluctuations of concentrations in the order of hundreds of ng/l for some PPPs and TPs, (iii) unexpected high concentrations (up to 220 ng/l) of a legacy compound (the fungicide oxadixyl withdrawn from the Swiss market in 2005). We hypothesized the cause of our findings was rooted in high PPPs levels in the shallow groundwater. To investigate this, we complemented our measurements with the long-term Swiss national monitoring program integrating samples over 14 days at the same location. The continuous long-term measurements found a few PPPs all year-round, thus indicating the presence of persistent contamination sources in the catchment. Next, we collected spatially distributed grab samples in tile drain outlets and stream water on a dry summer day in 2020. The dry-day campaign not only confirmed our hypothesis given the measured high concentrations of PPPs and TPs in tile drain outlets but also highlighted large spatial variability in measured concentrations along the stream. Hereafter, we highlight the questions that different monitoring schemes can answer in dry conditions. This information was relevant to observe for the first time, and thus foresee, the dynamic patterns of PPPs and TPs in the aquatic ecosystem in dry

summer conditions, with the latter generally becoming more frequent due to climate change.

#### KEYWORDS

pesticides, water quality, legacy contaminants, high-frequency monitoring, high resolution mass spectrometry, catchment, dry period, diel fluctuations

## 1. Introduction

Plant protection products (PPPs) use promises to achieve global food security (Popp et al., 2012), but the consequent environmental contamination poses a global environmental hazard (Stehle and Schulz, 2015; Maggi et al., 2020). It is the common view that surface waters are predominantly exposed to high concentrations of PPPs during rain events (Schulz, 2001; Szocs et al., 2017) and to transformation products (TPs) in dry periods (Rasmussen et al., 2015; Spycher et al., 2018; Belles et al., 2019; Sanford and Prosser, 2020; Halbach et al., 2021; Le Cor et al., 2021). Given the large effort that goes with sampling and analyzing PPPs from streams, many studies increase sampling frequency in response to hydrological proxies, such as rainfalls or increments in discharge in accordance with the scientific evidence showing that the largest loads of PPPs in water bodies occur during rain events (Doppler et al., 2012; Halbach et al., 2021). While proxy-triggered auto sampling seems to be a rational strategy, it nevertheless causes a bias underrepresenting dry weather conditions in PPPs studies. The available PPPs data may therefore reveal only a limited picture of the full exposure situation.

The consequences of a knowledge gap in PPPs and TPs exposure patterns in small streams can be of particular concern. Spycher et al. (2018) for example shows persistent high concentrations of PPPs and TPs in five agricultural streams during dry periods monitored by means of 12-h composite samples, pooled to a temporal resolution of several days. The subsequent analyses of individual 12-h subsamples reveal that concentrations in single subsamples could exceed the concentrations of pooled samples by up to a factor of 10. The causes for those high concentrations could not be clarified from 12-h composite samples. This knowledge gap can be detrimental for preserving the high ecological value of small streams (Biggs et al., 2016). Also, small streams constitute the majority of the channel length of river networks (Wohl, 2017). Salo et al. (2017) indicate that the persistence of natural aquatic populations was threatened by additive and interactive effects resulting from multiple anthropogenic changes, such as even low levels of chemical pollution and short-term heat waves. And yet, the vicinity of small streams to agricultural fields and their poor dilution capacity exacerbate their exposure to PPPs losses resulting from land and pest management (Szocs et al., 2017).

The significance of sources and flowpaths of PPPs and TPs to small streams can be identified by means of targeted monitoring studies (Neumann et al., 2002). In dry periods, potentially toxic concentration levels may arise from farmyard losses (Reichenberger et al., 2007), spray drift following applications (Schulz, 2004) or mishandling (Kreuger, 1998). It is known that irrigation can drive substantial leaching of herbicides from maize fields (Giuliano et al., 2021) and numerical modeling also supports the relevance of this practice to leaching (la Cecilia et al., 2020). Groundwater can be the carrier of PPPs and TPs stored in the catchment (Belles et al., 2019; Welch et al., 2019; Le Cor et al., 2021). Groundwater can also deliver legacy contaminants (Rasmussen et al., 2015), some of which may still be under mandatory monitoring in Europe due to their health and environmental risk as prescribed by the Water Framework Directive (EC, 2013) (e.g., the herbicide atrazine). Other physical drivers can deliver PPPs to surface water. For example, Messing et al. (2013) study the dry deposition of volatilised PPPs. Silva et al. (2018) show the potential of wind-eroded soil particles to contaminate surface water. Finally, Englert et al. (2017) develop a model to explain the translocation of systemic neonicotinoids from foliage to leaf litter material in streams.

In order to improve future water quality, a profound understanding of underlying contamination sources and processes within a catchment is required (Thomas et al., 2016). Previous knowledge of contamination sources and processes has typically been achieved by controlled PPPs application studies that continuously monitor the known PPPs sources as well as the water bodies receiving the mobilized PPPs (Leu et al., 2004; Schulz, 2004; Doppler et al., 2012; Lefrancq et al., 2017; Schönenberger and Stamm, 2021). The analytical workflow of processing monitoring samples is time-consuming, as it involves the collection of many water samples, transport to the laboratory, storage, preparation, analysis and quantification of target compounds. Additionally, traditional sampling techniques used in these studies, such as grab samples, time composite samples or passive samplers (Moschet et al., 2015), may only represent episodic peaks or constant concentrations. Inherently, traditional sampling techniques are not suitable to understand in detail PPPs dynamics during dry conditions, when contamination sources are expected to be not active. Such knowledge gap hinders the comprehensive assessment of PPPs and TPs dynamics in small streams leading to biased

monitoring strategies and risk mitigation approaches to protect aquatic ecosystems (Schulz, 2004).

In the companion study (la Cecilia et al., 2021), we present a first analysis of the novel continuous high-frequency dataset of PPPs and TPs acquired with the fully-automated, on-site high-resolution mass spectrometer platform *MS<sup>2</sup>Field* (Stravs et al., 2021). The first analysis focuses on wet periods. The second analysis is presented in this paper and made use of the same *MS<sup>2</sup>Field* dataset with a focus on dry periods. Additionally, we complemented the *MS<sup>2</sup>Field* dataset with two other datasets. The first complementary dataset was the continuous, low-frequency Swiss monitoring program. The second complementary dataset consisted of a follow-up dry-day field campaign. This latter involved collecting water samples from six point locations along the stream and four tile drain outlets. Using these three datasets, we report on the unexpected concentration patterns observed during two dry periods and on the spatial variability of contamination in shallow groundwater and its impact on surface water quality.

## 2. Methods

### 2.1. Study area

A small tile-drained agricultural catchment (2 km<sup>2</sup>) in the Swiss Plateau close to Lake Constance (Figure 1) was chosen for the continuous high-frequency *MS<sup>2</sup>Field* study (details on *MS<sup>2</sup>Field* in Section Monitoring campaigns). The choice was based on the results of a previous monitoring campaign (Spycher et al., 2018). The previous campaign revealed not only high PPPs and TPs concentrations but also substantial differences in concentration levels among 12-h composite samples in dry periods. The land use is mainly agricultural with urbanization below 1% and no wastewater treatment plant is present. There were slight changes in land use between 2019 and 2020, with more lands destined to corn and less areas covered with grasslands and orchards (visual and quantitative assessment in Supplementary Figure S1). The catchment is hilly with a median slope of about 3%. The catchment is drained by tile drains, which also connect an estimated additional surface of 0.7 km<sup>2</sup> to the stream (black lines in Figure 1; Source of the georeferenced vector file: Planimpuls.ch). Given the relatively high presence of PPPs-intensive crops and farmyards connected to the stream, the catchment is ranked at high risk of PPPs pollution potential, together with 10% of Swiss agricultural streams (Koch and Prasuhn, 2021).

### 2.2. Meteo-hydrological data

Water level was gauged by the cantonal environmental office at the outlet every 15 min. Rainfall data at 10 min resolution was obtained from the SwissMeteo measuring station “GUT” 1.8 km

from the outlet. In this research, we focused on dry periods referred to as days with no rainfall and a daily standard deviation of water levels smaller than 0.5 cm (to avoid falling levels of previous rainfalls).

### 2.3. Monitoring campaigns

We carried out two water quality assessment campaigns in the study area, one in 2019 and one in 2020. Between May 27<sup>th</sup> and July 7<sup>th</sup> in 2019 (41 days), we measured PPPs concentrations at high frequency (20 min) with *MS<sup>2</sup>Field* at the catchment outlet during wet and dry conditions (Table 1). The wet conditions are analyzed in la Cecilia et al. (2021).

In this research, we discuss the dry periods and expand the analysis of the national low-frequency long-term monitoring (NAWA-Trend) to highlight the seasonality and long-term temporal patterns of PPPs and TPs (Table 1).

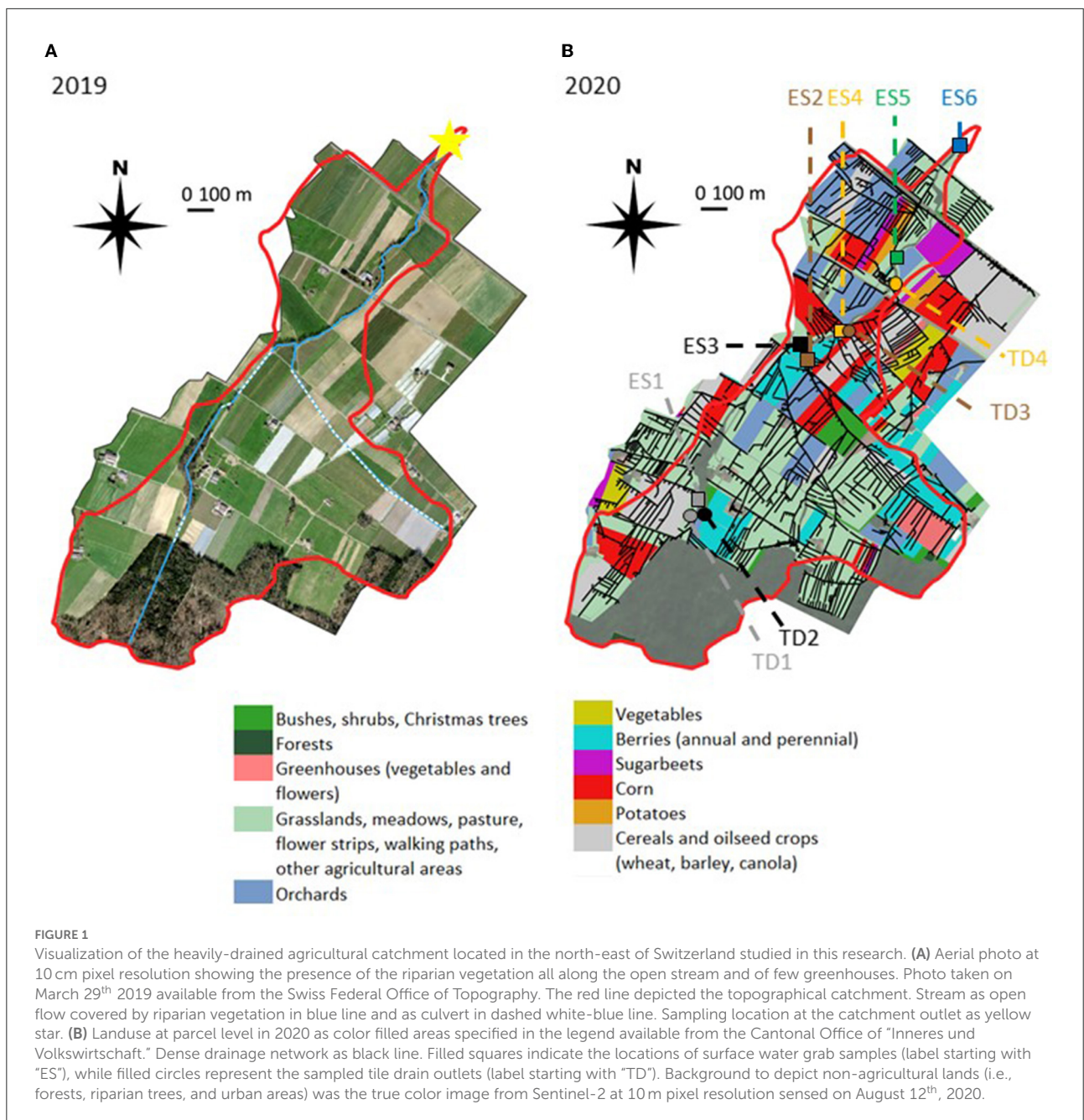
The spatial campaign occurred on August 12<sup>th</sup>, 2020 (Table 1). Grab samples were taken every 6 h at six locations along the stream network (filled squares with the label “ES” in Figure 1B, where “ES” is an identifier of the monitored stream) as well as from four tile drain outlets (filled circles with the label “TD,” which is the abbreviation of tile drain, in Figure 1B). One “ES” location coincided with the catchment outlet sampled in 2019. Pictures of the sampling locations are in Supplementary Figure S2.

#### 2.2.1. *MS<sup>2</sup>Field* in 2019

The fully automated mobile unit *MS<sup>2</sup>Field* was used to collect and analyse water samples at the catchment outlet by means of high-resolution mass spectrometry with limits of quantification in the low range of ng/l at 20 min time resolution. The workflow and further analytical aspects are explained in Stravs et al. (2021). *MS<sup>2</sup>Field* allows for target and non-target screening and target compounds typically differ from site to site depending on the expected contamination sources (e.g., agriculture, industry, cities). The *MS<sup>2</sup>Field* campaign covered part of the growing season of 2019, spanning from May 27<sup>th</sup> to July 7<sup>th</sup>, collecting 41 days of observations. This application resulted in 2,560 samples, which were analyzed for 60 compounds, of which 32 were measured in concentrations above the corresponding limit of quantification (LOQ). The PPPs and TPs dynamics relative to wet conditions are described in a companion article (la Cecilia et al., 2021). Hereby, we focused on novel PPPs dynamics observed in dry conditions.

#### 2.2.2. National low-frequency long-term monitoring (NAWA-Trend)

The catchment outlet in our study area was part of the Swiss National Surface Water Quality Monitoring Network



(Doppler et al., 2020). In the program NAWA-Trend, 3.5-days time-composite samples are collected during the spraying season between April-July (overlapping with the MS<sup>2</sup>Field campaign in 2019) and 14-days time-composite samples otherwise. Samples are collected with a MAXX sampler with cooling unit. After the composite sample is collected, it is stored in insulated boxes with freeze-packs and transported to the laboratory in Schaffhausen (INTERKANTONALES LABOR) for chemical analysis. Details on the chemical analyses are reported in the Supporting Information of la Cecilia et al. (2021) in Supplementary Section S2.

### 2.2.3. Spatial campaign in 2020

On August 12<sup>th</sup> 2020, we carried out a sampling campaign on a dry day, 4 days after the last rainfall, with the stream in low flow conditions. During the campaign, we collected water samples at 06:00, 12:00, 18:00 and at 21:00 (not 24:00 because a summer storm was approaching) at six different locations along the stream as well as from four outlets of active tile drains discharging into the stream. During the day, samples were kept at 4°C in an electric cooler and containing ice packs for 10% of the box volume. Within a few hours after the field campaign, samples were stored at -18 °C for 2 months until chemical analysis.



## 2.3. Chemical analysis of grab samples collected in 2020

The grab samples collected during the spatial campaign of 2020 were analyzed using direct injection liquid chromatography coupled to high-resolution mass spectrometry. The target list included 14 PPPs and two TPs (Supplementary Table S2). The compounds were selected based on three considerations. First, we targeted the PPPs and TPs that showed novel dynamics in the 2019's *MS<sup>2</sup>Field* campaign to verify whether they were reoccurring phenomena. Second, we included few other PPPs withdrawn from the Swiss market to assess their potential risk as legacy contaminants. Third, we targeted the TP of fluopyram, the latter being a persistent fungicide in this catchment to shed light on their environmental fate.

Standards of the target analytes were purchased and combined in a standard solution. The calibration standards (10–5,000 ng/l) were prepared by spiking the standard solution in nanopure water.

The frozen samples were thawed at room temperature. To homogenize the samples, they were swirled around and shaken. Then, 1.5 ml of each sample were transferred into 2 ml measurements vials. Each sample was centrifuged for 5 min at 4,800 rpm and 600  $\mu$ l of supernatant was transferred into another measurement vial.

To compensate for loss of substance during preparation and measurement, all samples and calibration standards were spiked with 30  $\mu$ l of a solution containing isotopically labeled internal standards (ISTD) at a concentration of 500 ng/l. Compounds and their corresponding ISTD have a very similar structure and are affected by potential degradation processes in the same way. The ratio of the signal of the target compound and the corresponding ISTD are therefore used for quantification. To account for matrix effects and assess relative recovery of the analytes, randomly selected samples were spiked with 50 or 500 ng/l of the standard solution.

Centrifugation, transfer, spiking of ISTD and standard solution were performed by a fully automated workflow (PAL RTC, CTC). Laboratory blanks and laboratory blinds were included in the measurement sequence to monitor instrument carry-over and contamination.

An injection volume of 100  $\mu$ l was used and chromatographic separation was performed on a reversed-phase C18 column (Atlantis T3, 3  $\mu$ m particle size, 3.0  $\times$  150 mm inner diameter, Waters), applying a water-methanol gradient (both containing 0.1% formic acid). The measurements were performed on a hybrid quadrupole-orbitrap mass spectrometer (Lumos Fusion, Thermo Scientific). Quantification of the target compounds was performed using the TraceFinder Software (Thermo Scientific). The samples were injected three times and the relative standard deviation was calculated for each sample for quality assurance. The software used for quantification

returned an error message instead of the concentration value for few injections. These no values were neglected from the calculation of the mean concentration and standard deviation of the few affected samples. The relative standard deviation was lower than 10% for 217 triplicates out of 240 from surface water and for 132 triplicates out of 140 from tile drain outlets (Supplementary Table S3). Relative standard deviations >10% almost always concerned triplicates with concentrations close to the corresponding LOQ.

LOQs were in the range of 5–20 ng/l and relative recoveries for 13 out of 15 compounds were in the range of 73–112%, while fluopyram had a relative recovery of 42% and diazinon of 69%.

## 2.4. Determination of the correlation between PPPs concentrations and water levels

We calculated the Pearson correlation coefficient ( $r$ ) between the concentration ( $C$ ) time series, and the water level ( $WL$ ) time series as  $r(t) = \frac{\text{cov}(WL(t+t), C(t))}{\sigma_{WL(t+t)}\sigma_{C(t)}}$  to include a lag time  $\Delta t$  between the time-series.

## 3. Results and discussions

In 2019 we identified two dry periods lasting in total 14 days (Figure 2). The first period spanned from June 2<sup>nd</sup> to June 8<sup>th</sup>, the second from June 25<sup>th</sup> to June 30<sup>th</sup>. Very low rainfall occurred in the 7 days before each of the two dry periods, summing to 6.9 mm and 4.9 mm, respectively.

In the next subsections, we first present the overall picture of the measured concentrations with *MS<sup>2</sup>Field* during the dry periods in 2019. Using the same dataset, we show novel concentration dynamics captured for few PPPs and TPs visible only with continuous high-frequency monitoring. For completeness, in Supplementary Section S4, we reported the dynamics of all PPPs and TPs having a concentration above their corresponding LOQ during dry conditions.

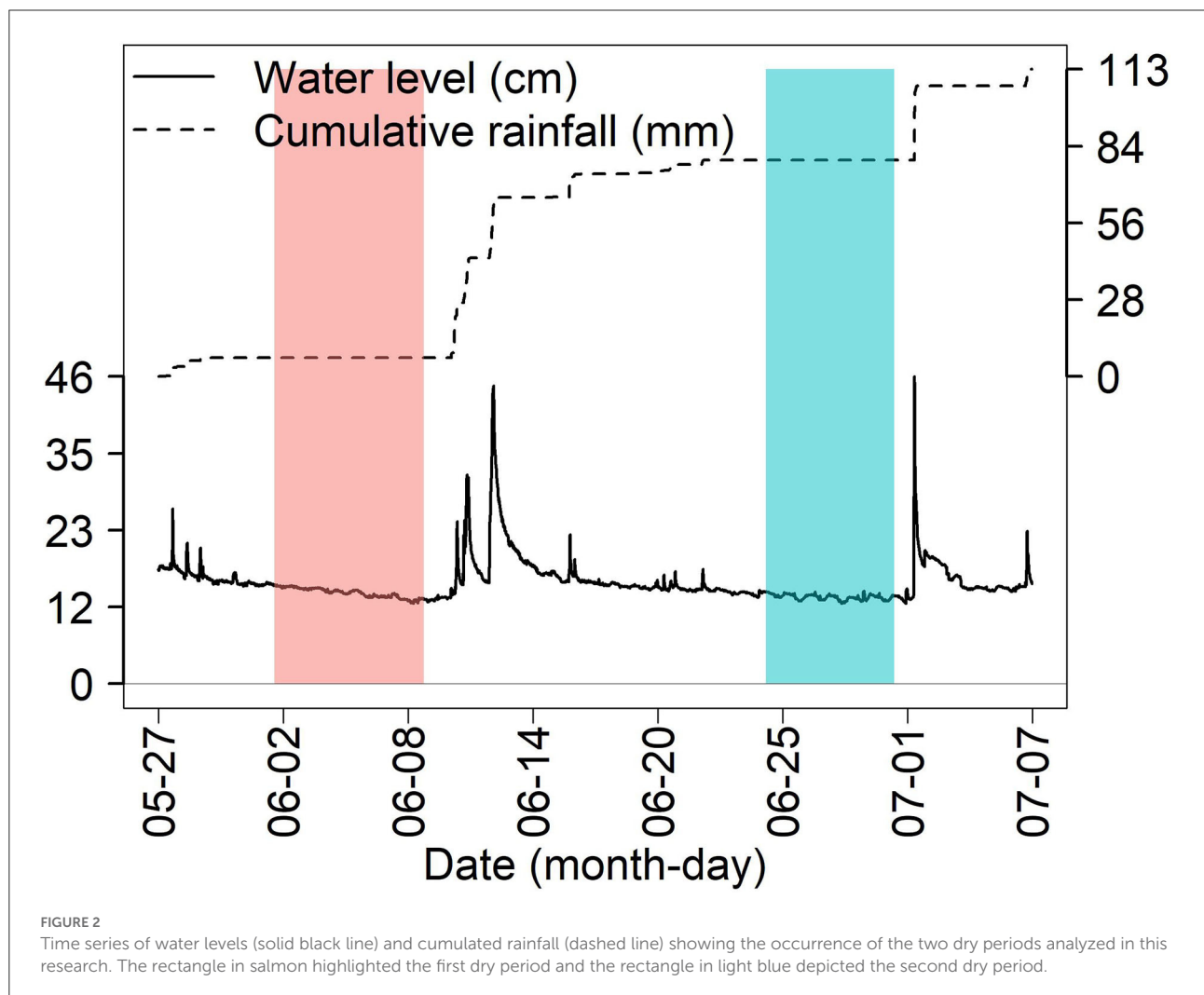
We analyse the continuous long-term NAWA-Trend data, which span over the years 2019, 2020 and 2021. The NAWA-Trend dataset allows for gaining further insights on the short-term high-frequency campaign of 2019. Finally, we present the results from the dry-day spatial campaigns of 2020.

### 3.1. Contaminant concentration magnitudes at high-frequency monitoring

Among the sixty target compounds, 19 exceeded their LOQ in these dry periods. The measured concentrations ranged from few ng/l values to 1,530 ng/l, covering three orders of

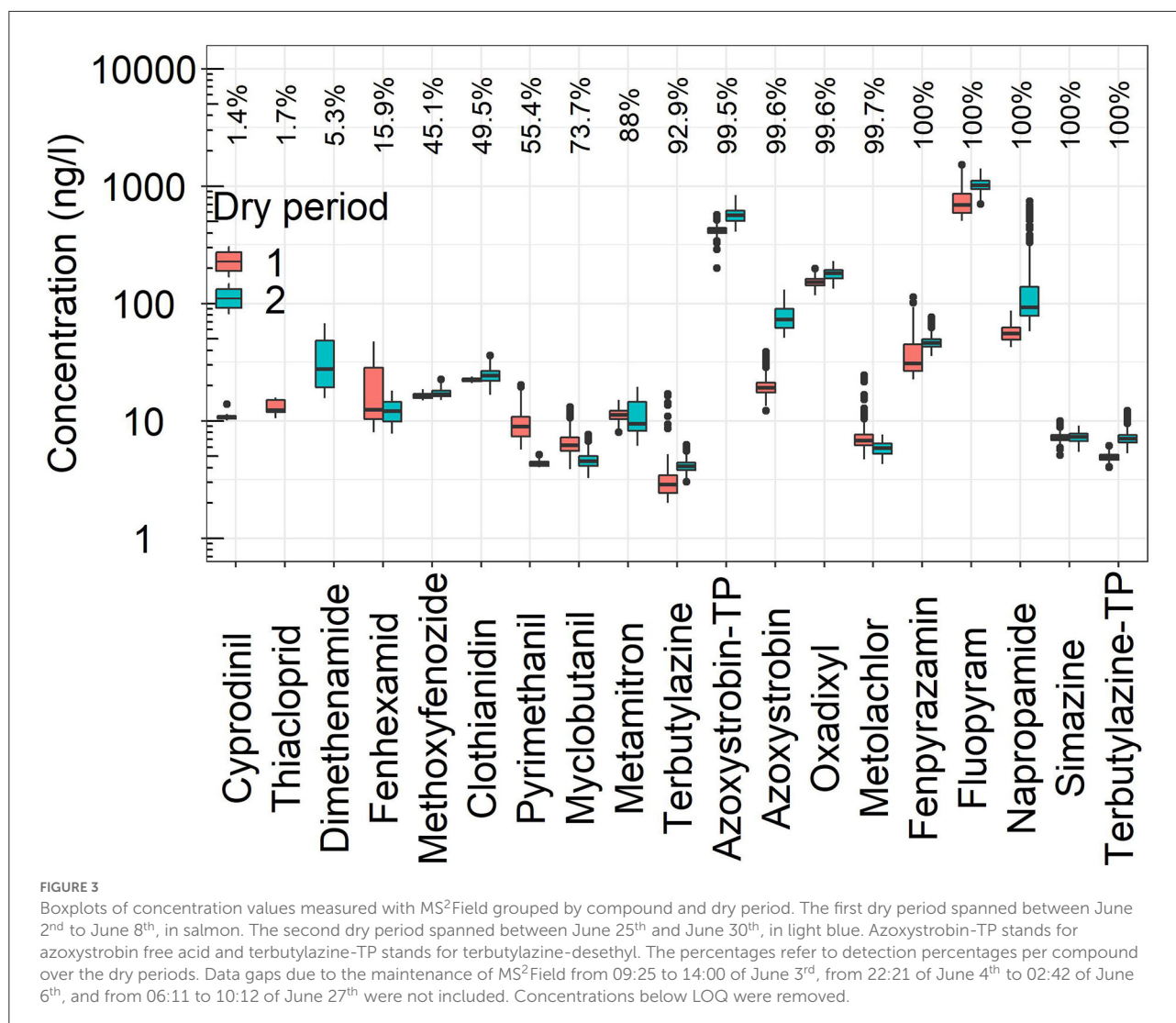
**TABLE 1** Overview of the sampling campaigns detailing the monitored time window, the location of the sampling, the type of sample collected and the temporal resolution of the campaign.

Campaign	Start date	End date	Sampling site	Sample type	Temporal resolution
MS <sup>2</sup> Field in 2019	27 <sup>th</sup> of May	7 <sup>th</sup> of July	Outlet	Grab sample	20 min
NAWA-Trend from 2019 ongoing	1 <sup>st</sup> of January	-	Outlet	Time-composite sample	3.5 days between April and July; 14 days, otherwise. For consistency, 3.5 days samples belonging to a 14 days period were averaged together.
Spatial campaign in 2020	12 <sup>th</sup> of August at 06:00	12 <sup>th</sup> of August at 21:00	6 surface water locations and 4 tile drain outlets	Grab sample	At 6:00, 12:00, 18:00, 21:00



magnitude (Figure 3). The PPPs, grouped by class, with the highest concentrations were the fungicide fluopyram (1,530 ng/l), the herbicide napropamide (740 ng/l) and the insecticide clothianidin (36 ng/l). Clothianidin is also a major TP of thiamethoxam. Azoxystrobin free acid (i.e., azoxystrobin’s TP) was measured at 830 ng/l. The high levels observed during

dry periods persisted until the following rain event. These concentration ranges confirmed earlier findings revealing high levels of fluopyram for example at the same location in 2015 (Spycher et al., 2018). We also found the fungicide oxadixyl at high concentrations throughout the dry periods with a maximum of 230 ng/l. Oxadixyl was withdrawn from the



Swiss market in 2005, 14 years before this study. The mean concentration of 13 compounds out of 19 increased from the first dry period to the second one (Figure 3). However, the mean water level did not substantially decrease being  $13.7 \pm 0.7$  cm in the first dry period and  $13.0 \pm 0.4$  cm in the second one. This indicated that the increase in concentrations were consequent to more recent PPPs applications rather than poorer dilution capacity.

### 3.2. Novel diel concentration fluctuations captured with the high-frequency monitoring

The high-frequency data demonstrated that few compounds underwent novel diel concentration patterns, lagging daily water level fluctuations by 6 to 8 h (Figure 4). We highlight that

not all PPPs and TPs showed diel concentration fluctuations, thus implying that the patterns were not an artifact of MS<sup>2</sup>Field (e.g., clothianidin in Supplementary Figure S3F, dimethenamid in Supplementary Figure S4B, metolachlor in Supplementary Figure S5F, oxadixyl in Supplementary Figure S6D and terbutylazine in Supplementary Figure S7B, among others). The concurrent and pronounced diel fluctuations of some PPPs and TPs persisted until the next rain event. Concentrations were higher at night and lower during the day. The highest intra-daily ratios between maximum and minimum concentrations over the second dry period ranged between 1.5 and 8.7 (Table 2). For compounds like napropamide, azoxystrobin, fluopyram and azoxystrobin-TP the fluctuations corresponded to changes of several hundreds ng/l between day and night. The concentrations of the fungicides azoxystrobin, fluopyram and fenpyrazamin fluctuated around a constant value, while the fluctuations of the herbicide napropamide dampened over the 1-week-long

dry period. The concentrations of azoxystrobin-TP showed a pronounced increasing trend. One reasonable explanation is that azoxystrobin was undergoing degradation to its TP, and the latter was building up in soil before reaching surface water.

We analyzed in detail the timing of minima and maxima of water levels and concentration levels of those PPPs and TPs showing diel fluctuations in the dry period. We chose the time window between June 25<sup>th</sup> and June 28<sup>th</sup> because the diel water level fluctuations were less affected by short-living water level peaks, which may be caused by other processes. Minimum water levels were measured between 15:15 and 17:00, while maxima from 20:15 and 22:15, with water levels increasing by about 1.8 mm per hour from the minima to the maxima (Table 3). Minimum concentration levels of PPPs occurred between 18:16 and 22:20, while maxima were measured from 00:59 to 06:03. The minimum  $r$  value (negative correlation) achieved a value of  $-0.80$  ( $p < 0.05$ ) given a lag time  $\Delta t \approx 8$  h for azoxystrobin-TP (Table 3). In these circumstances, the time series of water levels and chemical concentrations were almost in opposite phase (panels B in Supplementary Figures S8–S12). The maximum  $r$  value (positive correlation) was equal to  $0.59$  ( $p < 0.05$ ) given a lag time  $\Delta t \approx 20$  h for azoxystrobin (Table 3). In this case, the time series of water levels and chemical concentrations were almost synchronous.

The diel concentration fluctuations of some PPPs were probably the most surprising result. Diel patterns have also been observed for stream water quality parameters, such as pH and dissolved chemical species including oxygen, carbon, nitrogen due to diel changes in interplaying physical and biogeochemical cycles and processes (e.g., sunlight, respiration, photosynthesis, etc.) (Nimick et al., 2011). Instream geochemical processes including redox reactions and reversible adsorption could possibly explain the diel fluctuations of heavy metals in streams during low flows (Nimick et al., 2003). However, diel concentration fluctuations have not been reported for PPPs in streams not impacted by daily industrial discharges (e.g., wastewater treatment as in Stravs et al., 2021). We analyzed whether reported causes for diel fluctuations (Nimick et al., 2011) could explain our measurements. Napropamide as the PPP with the largest concentration fluctuations observed in Figure 4 could undergo fast photolytic degradation with a DT50 of 1.5 days (Lewis et al., 2016), but fenpyrazamin had the smallest concentration fluctuations despite a similar photolytic DT50 of 1.6 days. In addition, the daily timing and the well developed riparian vegetation rendered photolytic degradation a not very plausible reason for the diel fluctuations. Often the concentration started to decrease around midnight and well before sunrise. We hypothesized that the diel fluctuations of water levels and of PPPs and TPs concentrations were causally linked. Discharge and hence water level are known to vary due to evapotranspiration in the hillslope or in the riparian vegetation (Burt, 1979; Bren, 1997; Bond et al., 2002; Szeles et al., 2018; Harmon et al., 2020; Kirchner et al., 2020). We compared the water level observations against numerical

simulations for the studied catchment using a state-of-the-art fully integrated surface-subsurface hydrological model (i.e., CATHY by Camporese et al., 2010). The model achieved a satisfactory accuracy in capturing the streamflow dynamics over the 41-day-long monitoring period, with the Kling-Gupta efficiency index of 0.68, Nash-Sutcliffe model efficiency coefficient of 0.68, Willmott index of agreement of 0.88 and Root Mean Square Error of 0.04 (la Cecilia and Camporese, 2022). The results support the hypothesis that the sources of the diel streamflow fluctuations are transferred from the first meter of shallow groundwater to the stream, and that they are regulated by evapotranspiration in this small tile-drained agricultural stream during dry periods. Upon estimating the occurrence of two daily irrigation events to balance the water deficit between rainfall and evapotranspiration for all agricultural lands, with the first event at 7 a.m. and the second at 5 p.m., the simulations also reproduce the observed small short-living water level peaks (black line in Figure 4).

The results implied that the diel concentration fluctuations were caused by fluctuating fluxes from groundwater to surface water. We investigated whether PPPs with increasing sorption coefficient values resulted in increasing peaks arrival times. The data presented in Table 3 showed that to increasing  $K_{foc}$  values did not correspond an increasing arrival time of the peak concentration at night due to a stronger retardation effect. Yet, the order of the peaks timing among the target compounds changed during the 3 days considered in the analysis. This result indicated that sorption was not a predictor for the peaks arrival time. We then analyzed whether sorption could play a role in the lag time  $\Delta t$  needed to achieve the highest correlation, in magnitude. The data presented in Table 4 did not suggest the presence of a relationship between the four PPPs and the lag time  $\Delta t$ . While we acknowledged that more PPPs were needed to perform a robust analysis, we became more convinced that the peak arrival times were predominantly driven by other two predominant factors. One factor was the distance of the critical source areas from the outlet. The second factor was the temporal activation of the connectivity of the flowpath delivering contaminated groundwater to surface water. As a consequence, we suggest that knowledge on where these PPPs were applied would be key to pinpoint the critical source areas and where to further our understanding of transport processes as well as to suggest cost-effective risk management actions. In this sense, it would be crucial that research institutions have access to geo- and time-referenced PPPs application data to enhance the efficiency, effectiveness and scope of field studies.

### 3.3. Insights and outlooks from the continuous long-term monitoring

The monitoring opportunities achievable with *MS<sup>2</sup>Field* were unprecedented. In fact, *MS<sup>2</sup>Field* acquired a continuous high-frequency dataset of PPPs and TPs concentrations in dry



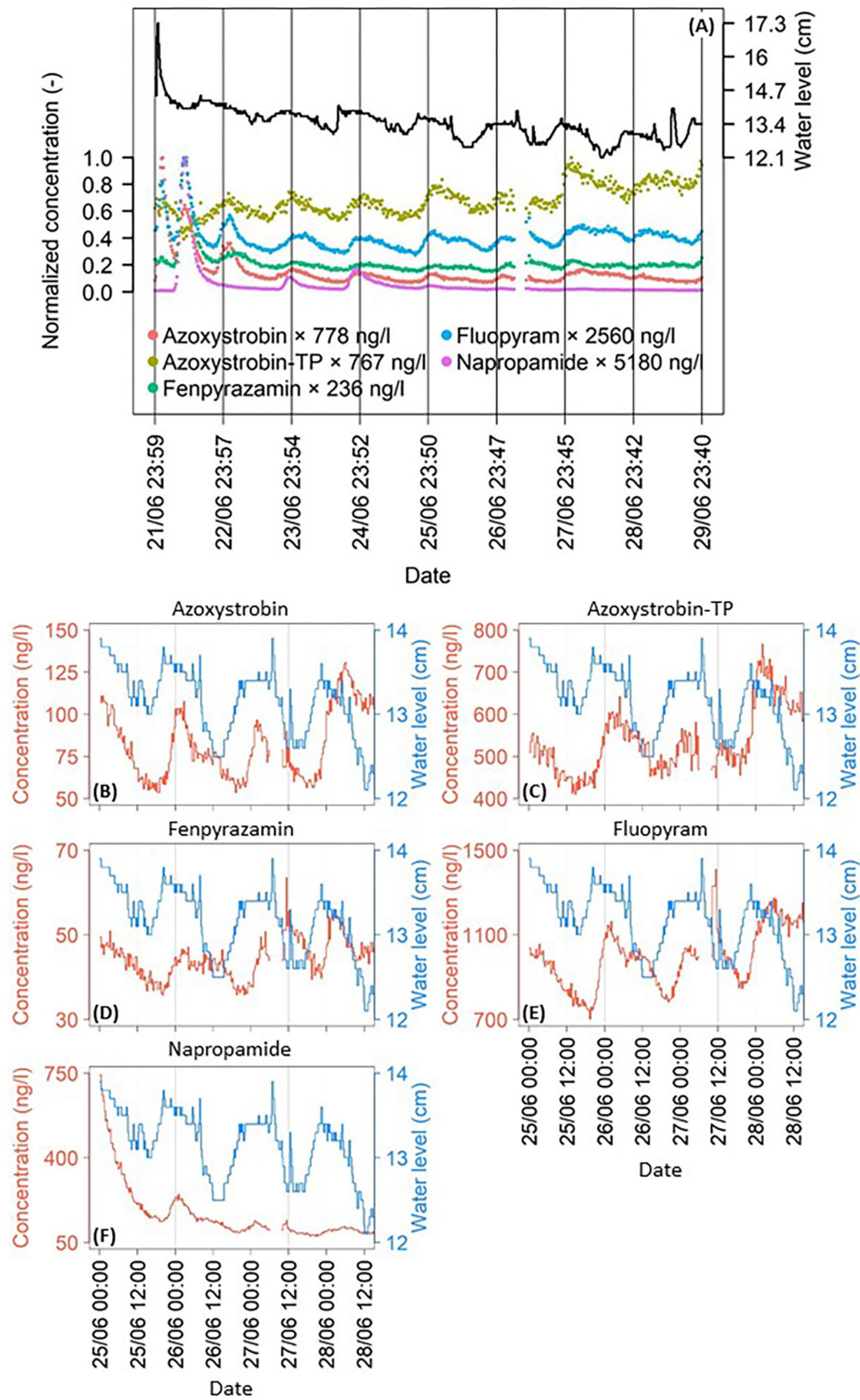


FIGURE 4

(A) Time series of PPPs and TPs normalized concentrations that showed diel fluctuations. Concentrations to be multiplied by the corresponding maximum value in the legend. The dash black line depicts the water level. No measurements on June 27<sup>th</sup> from 06:11 to 10:12 because the solution containing isotope-labeled internal standards had to be replenished. Concentrations below LOQ are not shown. Peaks in water levels

(Continued)

FIGURE 4 (Continued)

and concentrations on June 22<sup>nd</sup> are the result of a small rain event (further details on this event are provided in [la Cecilia et al., 2021](#)). Subpanels B–F depict the zoom in on panel A to highlight the temporal shift in daily minima and maxima between water levels and concentrations in the time window from June 25<sup>th</sup> to June 28<sup>th</sup>. Water levels shown in the right y-axis. (B) Azoxystrobin. (C) Azoxystrobin free acid. (D) Fenpyrazamin. (E) Fluopyram. (F) Napropamide.

**TABLE 2** Minimum and maximum concentrations in a 24-h period that resulted in the highest ratio between maximum and minimum during the second dry period.

Compound	Minimum—during the day (ng/l)	Maximum—during the night (ng/l)	Ratio	Date
Napropamide	100	870	8.7	June 24 <sup>th</sup>
Azoxystrobin	73	280	3.8	June 23 <sup>rd</sup>
Fluopyram	750	1,460	1.9	June 23 <sup>rd</sup>
Fenpyrazamin	41	70	1.7	June 23 <sup>rd</sup>
Azoxystrobin-TP	510	770	1.5	June 28 <sup>th</sup>

Tabulated are the compounds that followed diel fluctuations during the second dry period. The last column report the date when the highest ratio was reached.

conditions. However, it was neither the scope nor realistic to continue the high-frequency monitoring for months or years. And so, the NAWA-Trend program allowed for gaining further insights into our measurements thank to its continuous low-frequency monitoring.

The diel fluctuations (Figure 4) were not observed for all compounds during both dry periods. For example, such fluctuations were observed for the fungicide azoxystrobin in the second dry period only, while those of pyrimethanil in the first dry period (Supplementary Figure S3B and Supplementary Figure S6E, respectively). NAWA-Trend indicated that the diel patterns were evident in the periods of higher concentrations for the compounds of interest (Figures 5A, B). Very likely, the strength of the diel signal depended on the magnitude (contaminant mass) available at the critical source, the occurrence of the driving force (i.e., evapotranspiration) and the mixing with “contaminant-free” water contributed by other parts of the catchment.

NAWA-Trend revealed concentrations of the fungicide fluopyram exceeding 100 ng/l also in the winter season (Figure 5C); all other PPPs concentrations decreased below such level. This finding sparked the questioning of why fluopyram was continuously found in the stream. The first possible reason is that the physical-chemical properties are indicative of environmental persistence. This is based on high adsorption ( $K_{fOC} = 278.9 \text{ ml g}^{-1}$ ) and poor dissipation (DT50 of 309 days) parameters (Lewis et al., 2016). A second reason why fluopyram was detected at high levels also in winter may be grounded on its approved use in greenhouses as well as in apple orchards up to 1 week before harvest. In the studied catchment, variants of strawberries were grown early in the year below plastic tunnels, which could have required early treatments. Of course, the two reasons are not mutually exclusive.

The indication of a widespread and extended use all over the year of fluopyram in the catchment comes from application data (shared by farmers with the cantonal environmental office who kept the data confidential). The identified reasons for this widespread use are driven by the fungicide’s low toxicity against tested organisms under the current regulatory framework and its diverse use on crops grown in the catchment. The food supply chain also recommended to their consortium farmers to use the same PPP, which in this case was fluopyram, in order to avoid the multi-residue risk of PPPs in food and food commodities. And pip fruit growers did treat their apples before harvest (in autumn) to mitigate the risk of fruit rotting during storage, and therefore, secure their income up to the point of sale to any array of buyers. Because the choices for widespread fluopyram use grounded on local factors, such as expert recommendations, personal preferences and agricultural practices, it was the responsibility of the whole food value chain to undertake actions to reduce the use of PPPs in a more general context (as described in Möhring et al., 2020).

### 3.4. Dry-day field campaign in 2020

In 2020, NAWA-Trend was still measuring high levels of those PPPs that were measured at high concentrations and underwent diel concentration fluctuations in 2019. The dry-day campaign on August 12<sup>th</sup> 2020 generated three answers. First, it corroborated the previous findings of 2019 in terms of daily variability of concentration values. Second, it provided quantitative information on the spatial variability of concentration levels. Third, it assessed the contribution of tile drains to surface water contamination.

**TABLE 3** Timing of minima and maxima of water levels and of concentrations of those PPPs and TPs that showed diel fluctuations analyzed in the time window from June 25<sup>th</sup> to June 28<sup>th</sup>.

Variable	Kf <sub>oc</sub> geometric mean (ml/g)	Kf <sub>oc</sub> range (ml/g)	Time of minimum on June 25 <sup>th</sup>	Time of maximum on June 25 <sup>th</sup>	Time of minimum on June 26 <sup>th</sup>	Time of maximum on June 26 <sup>th</sup>	Time of minimum on June 27 <sup>th</sup>	Time of maximum on June 27 <sup>th</sup>
Water level	NA		16:15	20:15	15:15	20:15	17:00	22:15
Azoxystrobin-TP	-	-	14:35	04:40	18:07	04:50	18:59	02:02
Fluopyram	278.9	233–400	19:17	01:59	20:07	03:10	19:39	05:43
Fenpyrazamin	310	112–731	19:57	04:00	21:48	04:30	22:20	02:22
Azoxystrobin	423	207–594	18:16	02:39	19:07	01:49	19:39	06:03
Napropamide	885	409–1,593	19:37	00:59	20:27	01:09	22:00	05:43

Rows sorted by Kf<sub>oc</sub> geometric mean reported in Lewis et al. (2016). Kf<sub>oc</sub> range in the European Food Safety Authority's conclusions on PPPs peer review (EFSA, 2010a,b, 2012, 2013). NA stands for Not Applicable (Water level). Kf<sub>oc</sub> not reported for azoxystrobin-TP.

**TABLE 4** Correlations between time series of water level and compounds that showed diel concentrations fluctuations during the second dry period.

Pair of variables	Kf <sub>oc</sub> geometric mean (ml/g)	Kf <sub>oc</sub> range (ml/g)	Minimum <i>r</i> ( <i>p</i> -value)	Lag time for the minimum <i>r</i> (hours:minutes)	Maximum <i>r</i> ( <i>p</i> -value)	Lag time for the maximum <i>r</i> (hours:minutes)
Water level –Azoxystrobin-TP	-	-	−0.80 (3.7 × 10 <sup>−54</sup> )	9:04	+0.26 (1.4 × 10 <sup>−4</sup> )	21:48
Water level-Fluopyram	278.9	233–400	−0.70 (1.0 × 10 <sup>−37</sup> )	7:43	+0.28 (4.7 × 10 <sup>−5</sup> )	19:48
Water level-Fenpyrazamin	310	112–731	−0.44 (2.7 × 10 <sup>−13</sup> )	5:42	+0.13 (4.5 × 10 <sup>−2</sup> )	17:45
Water level-Azoxystrobin	423	207–594	−0.68 (1.2 × 10 <sup>−33</sup> )	8:23	+0.59 (7.4 × 10 <sup>−21</sup> )	20:28
Water level-Napropamide	885	409–1,593	+0.17 (8.6 × 10 <sup>−3</sup> )	9:04	+0.59 (8.5 × 10 <sup>−21</sup> )	19:48

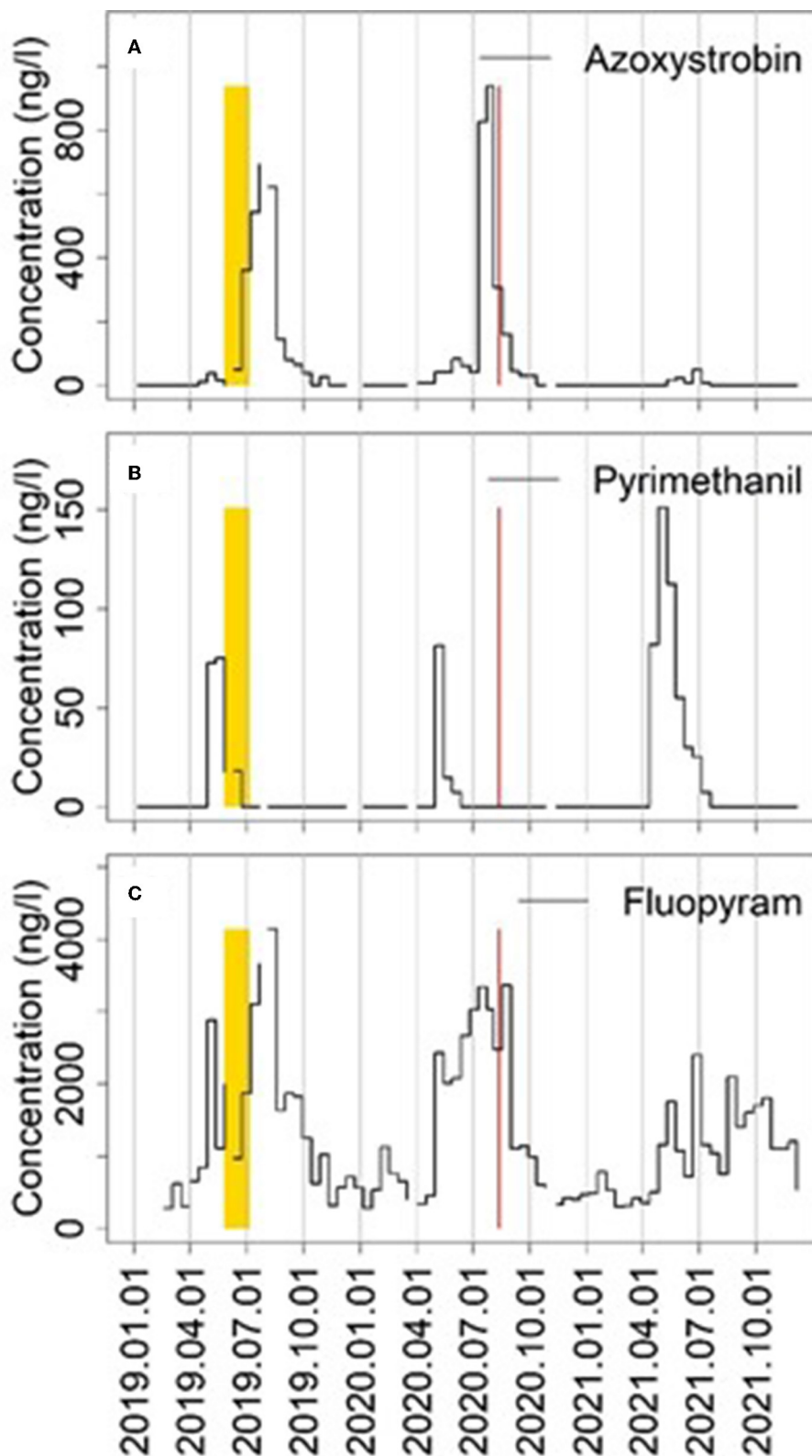
Minima and maxima of the Pearson correlation coefficient *r*, with the *p*-value in brackets, considering a lag time between the study variables. Lag time in hours and minutes of the water level with respect to the paired compound that resulted in the minima and maxima *r* values. The determination of the lag times yielding the minimum and maximum *r* values is detailed in Supplementary Section S5. Rows sorted by Kf<sub>oc</sub> geometric mean reported in Lewis et al. (2016). Kf<sub>oc</sub> range in the European Food Safety Authority's conclusions on PPPs peer review (EFSA, 2010a,b, 2012, 2013). Kf<sub>oc</sub> not reported for azoxystrobin-TP.

### 3.4.1. Surface water

Seven PPPs and two TPs exceeded their LOQ out of the 16 target compounds in the stream (Supplementary Figure S13). The concentrations at the outlet were in line with the measurements of 2019 (blue filled circles in Figure 6 and Supplementary Figure S13 representing the location ES6). Along the stream, concentrations ranged from below LOQ to 3,300 ng/l, the latter being the maximum value measured for the fungicide fluopyram (Figure 6A). These measurements corroborated the high levels observed during dry periods of the previous years. Maximum concentrations were generally reached in the two most upstream sampled locations, with the right branch (brown filled circles in Figure 6 and Supplementary Figure S13 representing ES2) being more contaminated than the left one (gray and black filled circles in Figure 6 and Supplementary Figure S13 representing ES1 and

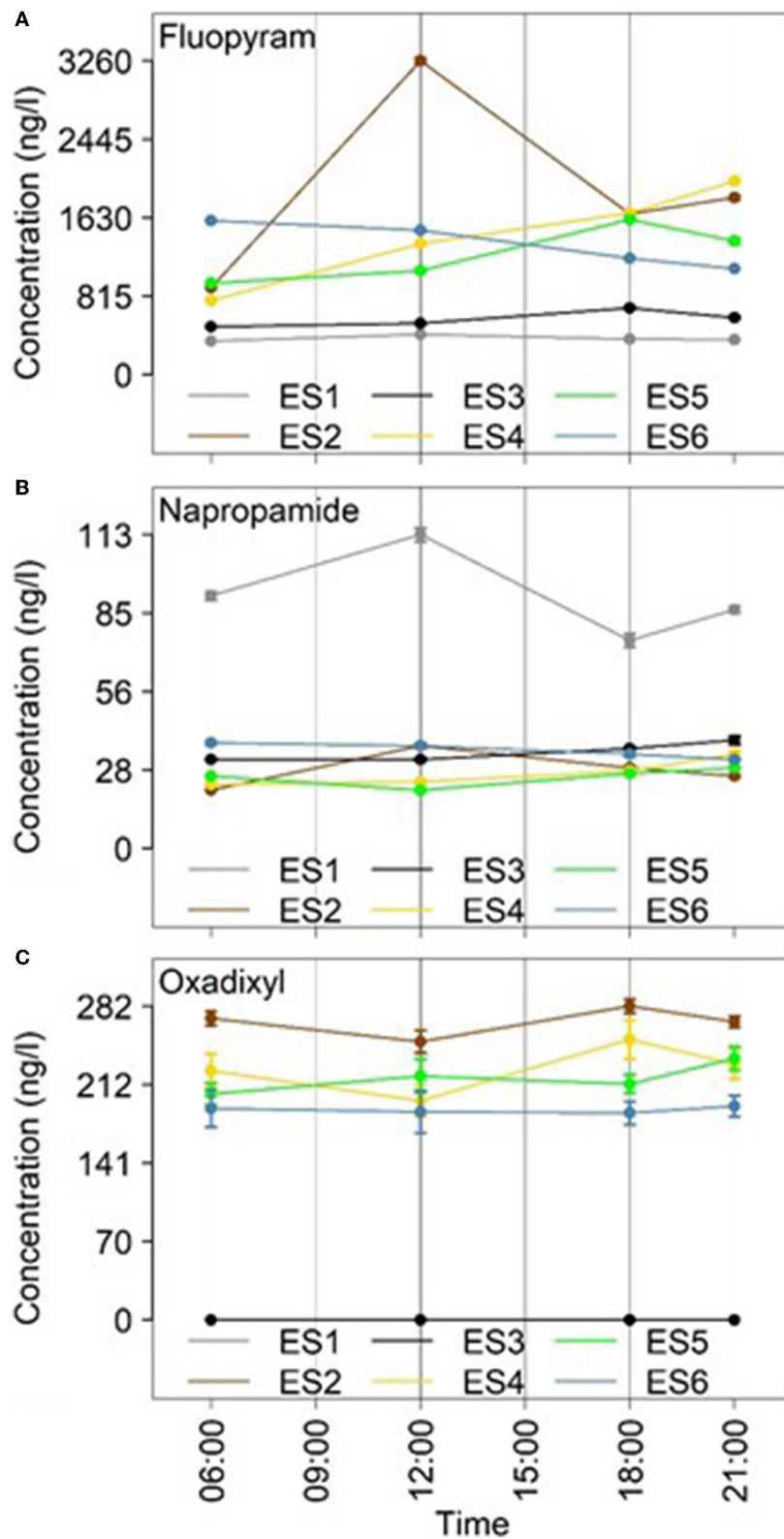
ES3, respectively). This may be explained by the larger cultivated area draining into the right branch (Figure 1). Note that the right branch is a culvert before reaching the junction with the left branch, and it is fed by a dense drainage network. Therefore, the spatial campaign could also allow for retrospectively distinguishing the contamination sources coming from the left and right branches. Importantly, oxadixyl concentrations were below its LOQ in the left branch of the stream and decreased along the stream from the right branch to the outlet (Figure 6C).

The different PPPs reached their maximum concentrations in different locations and at different times (Supplementary Figures S14, S15). The ratio between the maximum and minimum concentration for a single PPP measured at the same time but at different locations reached a factor of 17, with a mean value > 4 among the PPPs. The ratio between the maximum and minimum concentrations for



**FIGURE 5**  
 Time series of the concentrations of selected PPPs measured by NAWA-Trend at 14 days resolution. The continuous low-frequency monitoring allowed for understanding the seasonal patterns of target PPPs. The yellow background highlighted the relatively short time-window covered by the high-frequency monitoring campaign with MS<sup>2</sup>Field in 2019. The red background visualized the period of the dry-day sampling campaign of August 12<sup>th</sup>, 2020 (thickness cover 3 days rather than 1 day for visualization purposes). (A) Fungicide azoxystrobin, (B) fungicide pyrimethanil, and (C) fungicide fluopyram.





**FIGURE 6**  
 Time series of concentrations in surface water for selected PPPs measured during the dry-day campaign across the catchment on August 12<sup>th</sup> 2020. Data points are grouped by compound, colored 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). (A) Fungicide fluopyram, (B) herbicide napropamide, and (C) fungicide oxadixyl withdrawn from the Swiss market in 2005.

a single PPP at one location over the day exceeded a factor of 4, with a mean value of 1.6 among the PPPs. For example, azoxystrobin concentrations ranged between a minimum of 10 ng/l to a maximum of 120 ng/l at 6:00 across the catchment as well as ranged between a minimum of 49 ng/l at 6:00 to a maximum of 200 ng/l at 12:00 at the same location. These results confirmed that concentrations can vary during the day at all locations during low flow conditions. This variability could be due to land management practices triggering contamination sources and transport (i.e., PPPs applications, irrigation, etc.) but also due to natural diel fluctuations as shown in this research.

The measurement of a few grab samples spatially distributed proved to be an agile, efficient and effective strategy to narrow down influential contamination sources. Successful results for sources identification by means of non-intensive spatial monitoring are also obtained by Warner et al. (2021). Our monitoring relying upon previous knowledge about diel fluctuations in dry periods further revealed the large variability per compound depending on the time of the day. Some PPPs reached very high concentration levels. The most extreme case was fluopyram, which high concentrations corroborate earlier findings from the study area (Spycher et al., 2018) but are way beyond what has been reported in the limited literature reporting fluopyram concentrations (Sjerps et al., 2019; Pinasseau et al., 2020). What the grab sampling though clearly demonstrated was the occurrence of fluopyram in the entire length of the open stream and in several tile drains. Thus, the transport pathway had to be widespread across the catchment, which was in agreement with our discussion on fluopyram use in Section Insights and outlooks from the continuous long-term monitoring. Due to confidentiality, we could not study the relationship between PPPs applications and their detections in the stream. It is known that PPPs applications, environmental drivers and timing of sampling are important factors for explaining PPPs detections in water (Materu et al., 2021; Schönberger et al., 2022). Yet, mitigation measures may be effective at reducing water pollution by attenuating the mobilization and transport of PPPs (Chow et al., 2020). In this catchment, the reduced use of persistent PPPs is suggested for avoiding long-term contamination of the stream, such as in the case of oxadixyl. In fact, very likely the high concentrations of the legacy compound oxadixyl reflects the impact of lateral flow of a fungicide intensively used in the past. While fluopyram was not yet a concern for surface water due to its low acute toxicity profile (against the tested organisms), it posed a risk to groundwater where the safety threshold was more stringent and equal to 100 ng/l. The aquatic ecotoxicological assessment revealed no exceedances by the approved PPPs of the corresponding acute quality standards (AQS) listed in the Swiss legislation. However, for azoxystrobin-TP and fluopyram-TP we did not have their corresponding AQS. If we were to use the AQS of the corresponding parent

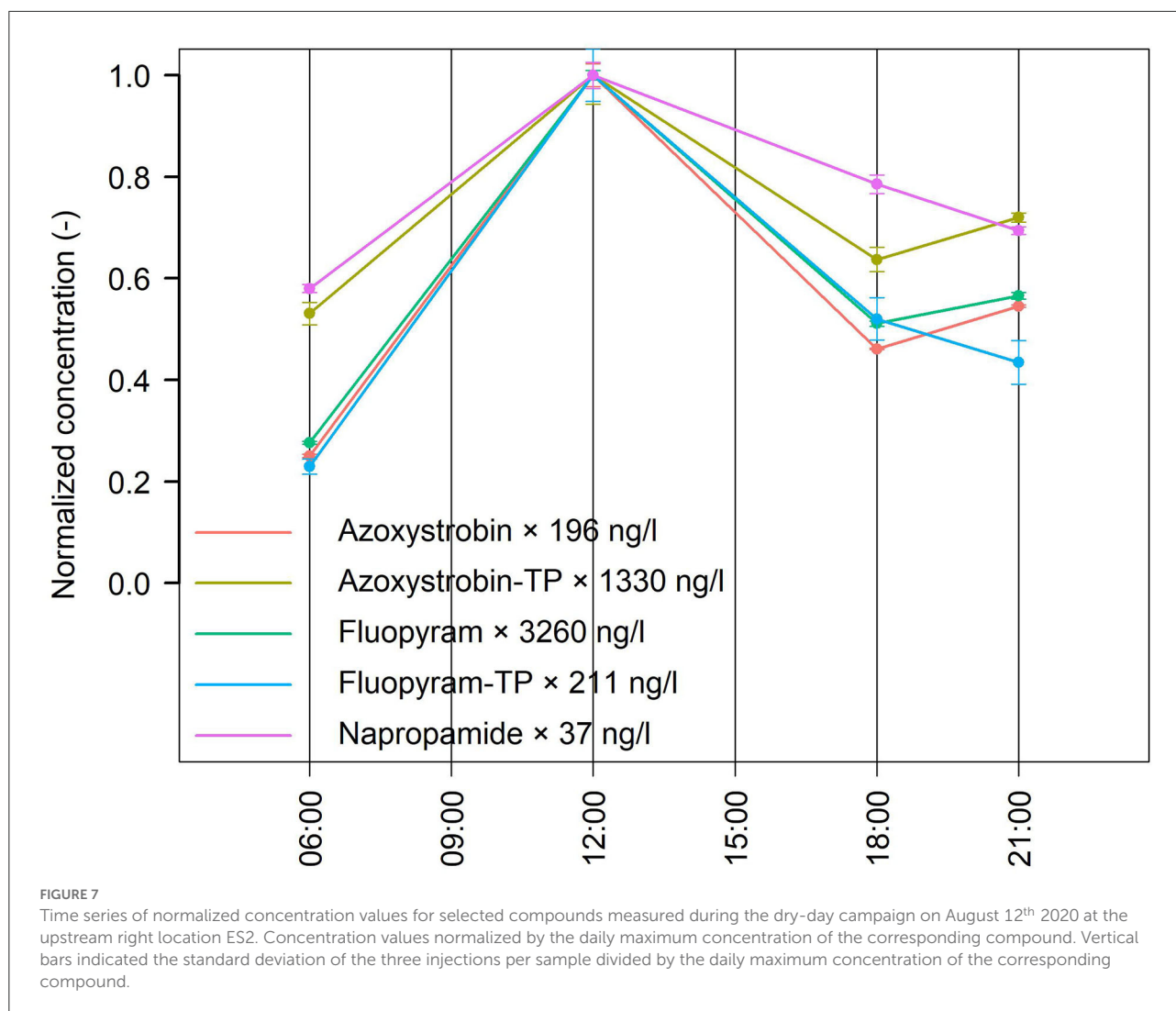
compound, then azoxystrobin-TP poses a risk to the aquatic environment. In fact, we calculated a mean concentration over the day and over the sampling locations of 706 ng/l, which is greater than the AQS of azoxystrobin equal to 550 ng/l. Fluopyram-TP concentrations did not exceed the AQS of fluopyram, and therefore, is supposed not to pose a risk to aquatic organisms. For oxadixyl, there is a published *ad-hoc* ecotoxicological standard (Maximum Tolerable Risk or MTR) value of 109  $\mu\text{g/l}$  (Beek et al., 2008). The MTR value of oxadixyl is about three orders of magnitude higher than the measured concentrations. We concluded that oxadixyl does not pose a risk to the aquatic environment.

### 3.4.2. Diel fluctuations

At the catchment outlet (ES6), those PPPs with concentrations showing diel fluctuations in 2019, were again measured at higher concentrations at 6:00 and lower concentrations at 21:00 in 2020 (fluopyram in Figure 6A and azoxystrobin together with their corresponding TPs in Figure 7). This result demonstrated that diel fluctuations were a re-occurring phenomenon in this catchment. The data from 2020 further showed that also fluopyram-TP followed diel fluctuations, which was not analyzed in 2019.

In the right branch (ES2), we observed a clear peak for fluopyram, azoxystrobin and their TPs at 12:00, with concentrations 2 to 4 times higher than the concentrations measured at 6:00 or 18:00 (fluopyram in Figure 6A and azoxystrobin together with their corresponding TPs in Figure 7), with the lack of meteorological drivers. However, it seemed not plausible that the branch ES2 is the source of the diel fluctuations given the long travel time of 12 h for the peaks measured at 12:00 to reach the outlet at night (only 1 km downstream).

An insightful analysis resulted from the calculation of normalized concentrations with respect to the maximum concentration relative to each compound. Interestingly, the slopes of the changes in normalized concentrations for azoxystrobin and fluopyram were identical over the day (Figure 7). Because this would indicate an identical mixing ratio at different times, we inferred that they were delivered by the same source. A similar result was found for fluopyram-TP although in the last sample the slope was negative for fluopyram-TP in contrast with the positive slope for azoxystrobin and fluopyram. The slopes of the changes for azoxystrobin and fluopyram were aligned with the ones of azoxystrobin-TP, but azoxystrobin-TP normalized concentrations varied less than the former PPPs, which may suggest the steadier mobilization of azoxystrobin-TP from its source and flowpath than azoxystrobin and fluopyram. The initial slope of the changes for napropamide was identical to azoxystrobin-TP but differed in the following times.



### 3.4.3. Tile drains

The tile drain samples confirmed results observed in the stream: some compounds were found at elevated concentrations despite the dry conditions. Concentrations achieved for example a maximum value of 490 ng/l by fluopyram (Table 5; Supplementary Figure S16).

By overlaying the drainage network map with the high-resolution land use maps of 2019 and 2020, we could verify that the measured substances in TD1 matched with the PPPs allowed for use in the previous or current year on the drained areas according to the Swiss legislation (Table 5). However, we could not use the land use data to confidently shortlist the PPPs to measure at the outlets of drainage networks. This is because often tens of PPPs are approved for the same land use, intercropping within a year or crop rotations between years can be a management practice and the drainage network can encompass many land uses. The second outlet was not recorded in the acquired georeferenced vector file

of the drainage network (black lines in Figure 1B; Source: Planimpuls.ch). Therefore, we could not carry out the same matching procedure.

Through the inspection of the tile drain outlets, we observed that branches of the stream network were active in dry conditions only thanks to the contribution of culverts fed by tile drains. In particular, the left branch of the stream was formed by three tile drains, and two of them (TD1 and TD2) were active during the campaign. Thus, assuring good water quality in tile drains can be relevant for the ecological status of small streams.

Downstream of the junction between the left branch and the right one, we found two additional active tile drains, TD3 upstream and TD4 downstream. Interestingly, TD3 and TD4 also drained areas outside the topographic catchment. In TD4, the external area extended to 6.6 ha. We measured higher concentrations in TD4 than in TD3. This result stressed the fact that processes occurring outside the topographic catchment can be relevant to understand water quality issues in small

TABLE 5 Maximum concentrations of the target compounds measured at the tile drain outlets during the dry-day campaign in 2020.

Identifier of the tile drain outlet (TD) in 2020	Landuse overlaying the TD network in 2019	Landuse area overlaying the TD network in 2019 (m <sup>2</sup> )	Landuse overlaying the TD network in 2020	Landuse area overlaying the TD network in 2020 (m <sup>2</sup> )	Compound targeted in 2020	Maximum concentration at TD in 2020 (ng/l)	Timing of the maximum concentration (hour of the day)
TD1	Strawberries	9,172	Strawberries	9,172	Azoxystrobin	9	18
	Perennial berries	6,715	Perennial berries	6,715	Azoxystrobin-TP	160	22
	Autumn wheat	20,654	Autumn wheat	19,998	Fluopyram	270	6
	Apple orchard	5,383	Apple orchard	5,383	Fluopyram-TP	32	6
	Pear orchard	4,203	Pear orchard	4,203	Napropamide	63	6
	Corn	19,959	Corn	38,689	Simazine	10	18
	Barley	18,730	-	-			
TD2	-		-		Azoxystrobin	12	6
	-		-		Azoxystrobin-TP	348	22
	-		-		Clothianidin	77	18
	-		-		Fluopyram	495	18
	-		-		Fluopyram-TP	52	12
	-		-		Napropamide	130	6
	-		-		Simazine	8	22
TD3	Perennial berries	18,985	Perennial berries	18,985	Azoxystrobin-TP	42	12
	Other orchards	12,336	Other orchards	12,336	Clothianidin	14	12
	Corn	10,389	Corn	13,430	Fluopyram	76	12
	Corn as ensilage	25,224	Corn as ensilage	18,671	Fluopyram-TP	6	12
	Wheat as forage	21,768	-		Oxadixyl	190	22
	-		Strawberries	12,014			
	-		Barley	21,768			
TD4	Forcing houses	8,072	Forcing houses	8,072	Azoxystrobin	9	18
	Autumn wheat	33,028	Autumn wheat	33,027	Azoxystrobin-TP	410	18
	Corn as ensilage	7,256	Corn as ensilage	18,253	Fluopyram	340	12
	Vegetables	30,413	Vegetables	25,024	Fluopyram-TP	10	12
	Sugarbeet	18,253	-		Metamitron	13	18
	Potatoes	2,382	-		Oxadixyl	51	22

The tile drains are linked with the corresponding drained land uses (m<sup>2</sup>) reported in the georeferenced tile drainage network vector file. The table excludes the contribution from meadows and pastures. The land use above TD2 was not listed because it was not reported in the drainage network vector file.



streams. Also in this case, the measured PPPs matched with the approved PPPs for the land uses drained by TD3 and TD4 (Table 5).

## 4. Conclusions

Water quality protection and improvement of the aquatic ecosystem is urged worldwide. As the likelihood of dry conditions in agricultural streams is increasing due to climate change, it is important to close the knowledge gap on the dynamics of plant protection products (PPPs) and their transformation products (TPs) under these conditions. By analyzing the novel continuous, high-frequency and multi-compound monitoring dataset gained by means of *MS<sup>2</sup>Field*, this study revealed diel concentration fluctuations for some PPPs and TPs over extended periods, with maximum concentrations occurring at night. Crucially, grab sampling is not typically carried out at night, when concentrations can be higher than during the day in dry conditions. Very likely, the diel patterns originated from evapotranspiration-driven diel fluctuations in groundwater flow into surface water. This suggests that PPPs and TPs persisted in the shallow groundwater. Groundwater level and quality data above and below the tile drain network would be important to better understand the mechanisms involved in the generation of the diel fluctuations. In case the systemic contaminants were to be found within the root zone, it would also be likely that plants took them up stored them in their tissues such as leaves.

A knowledge-based non-intensive spatially-distributed grab sampling campaign of surface water was effective to corroborate the diel fluctuations of concentrations, demonstrate the widespread occurrence of high concentrations of some fungicides in the catchment as well as narrow down persistent contamination sources. Adding the sampling of tile drains allowed for identifying where this flowpath was relevant for water quality issues, which corroborated the widespread contamination of the shallow groundwater by some fungicides.

Open land use data explained the PPPs measured in the below tile drains. However, land use data were not suitable to shortlist the PPPs to measure at the outlets of drainage networks given that often tens of PPPs are approved for the same land use, crops can be rotated, farmers can have intercrops and the drainage network can encompass many land uses.

To address the issue of the generality of the findings, more evidence is needed to understand the drivers of the persistent contamination sources that led to the unexpected dynamics in low flow conditions. Technology is delivering data of unprecedented quality in terms of continuity and frequency. However, accurate insights from such innovative campaigns is dependent on complementary evidence resulting from stakeholder's decision-making and

activities, which information may be difficult to acquire. Thus, it is crucial to foster collaborative monitoring initiatives among stakeholders to achieve safer PPPs risk management, when alternative pest management solutions not relying on synthetic chemicals would not be effective.

## Data availability statement

Data presented in this article is available at <https://opendata.eawag.ch/group> under the project NAWA-Flowpath. The MS<sup>2</sup>Field data is published as open data on the Eawag digital repository with the doi: [10.25678/0007BD](https://doi.org/10.25678/0007BD).

## Ethics statement

Written informed consent was obtained from the author DC for the publication of any potentially identifiable images or data included in this article.

## Author contributions

HE, MK, HS, and CS contributed to conception and design of the *MS<sup>2</sup>Field* study. DC, MK, HS, and CS contributed to conception and design of the grab sampling campaign. HE and MK maintained active exchanges with local stakeholders. AD performed the chemical analyses and wrote sections of the manuscript. DC and AD organized the database. DC performed the data analysis and wrote the first draft of the manuscript. HS and CS substantially contributed to shaping the manuscript until its final version. All authors contributed to manuscript revision, read, and approved the submitted version.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/frwa.2022.1062198/full#supplementary-material>

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