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## High-concentrations diel-fluctuations of Plants Protection Products in dry periods

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Modern agriculture routinely uses Plant Protection Products (PPPs) to guarantee food security. However, PPPs can reach surface waters where they pose a threat to susceptible non-target organisms. Understanding the contamination sources and flowpaths is of utmost importance to design optimal pollution mitigation strategies. While highest concentration peaks typically occur during rainfalls following PPPs applications, a monitoring campaign in a small Swiss agricultural stream in 2019 detected several compounds in concentrations exceeding the precautionary limit of 100 ng/l by up to 14 times during a dry period. The further exploration of the time series revealed for the first time diel fluctuations of some PPPs. Such peculiar patterns excluded the occurrence of known contamination pathways including spray drift, wind erosion and dry deposition. Despite the availability of an unprecedented high-temporal resolution dataset, we were not able to disentangle the source-flowpath combination driving the observed peculiar dynamics.

Here we present the results of the follow-up 1-day field campaign aiming to close this knowledge gap. The campaign was carried out on the dry day of August 12<sup>th</sup> 2020 and we collected water samples every 6 hours from the stream at 6 different locations and from 4 outlets of active tile drains.

The results revealed widespread contamination by the fungicide fluopyram; its transformation product fluopyram-benzamide followed identical dynamics but its concentration was 10 times lower than the parent compound. This result is in line with the high DT50 of fluopyram and its broad use in the catchment. The data showed that diel fluctuations were a reoccurring phenomenon; concentrations were higher in the early morning and lower in the early evening at the most downstream location. However, the fluctuating PPPs showed a concentration peak in the upstream location at midday. We were able to narrow down the contamination sources of napropamide, clothianidin, and oxadixyl; the first is a current herbicide, the second is an insecticide not reapproved since 2020, while the third is an old fungicide banned in Switzerland in 2005, which we measured at approximately 200 ng/l. Finally, the investigated tile drains delivered PPPs at lower concentrations compared to the levels measured in the surface water, with the exception of the herbicide metamitron, which was measured at nearly 20 ng/l only at the outlet of

1 tile drain.

The presented research suggested that contamination sources can be localized by means of grab samples collected along the stream. However, it was not conclusive on the flowpath delivering PPPs to the stream. We hypothesize that 2 processes may explain the reported patterns: (i) irrigation at the upstream locations in the early morning; (ii) intra-daily exchanges at the interface between surface water and contaminated shallow groundwater. We will complement the study with expert knowledge by local stakeholders, satellite-derived soil moisture indices, high-resolution land use data and regulatory information to establish a methodology to optimally identify critical source areas in dry periods, where mitigation strategies should be put in place.