

EGU2020-9601

<https://doi.org/10.5194/egusphere-egu2020-9601>

EGU General Assembly 2020

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Continuous high-frequency pesticides monitoring reveals underestimated environmental threats and unique insights into transport patterns

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Plant protection products (PPPs) are used routinely in modern agriculture and they can reach surface waters from treated fields or equipment handling areas. Assessing water contamination for a broad set of PPPs is challenging due to the episodic occurrence of concentration peaks. The traditional workflow of taking samples in the field, transferring to the lab, possible storing, and sample preparation and analysis strongly limits sampling frequency and duration of sampling campaign, in particular for labile PPPs.

Here we present for the first time results from the on-site platform MS²field quantifying hundreds of PPPs with 20 minutes temporal resolution continuously yielding concentrations in real-time. MS²field is a fully automated mobile unit to be deployed in the field, where it collects water samples and performs target and non-target high-resolution mass spectrometry with limits of quantification in the low range of ng/l. For the presented application, MS²field was deployed in a small agricultural catchments in 2019 (May – July, 41 days of observation) in the Swiss Plateau close to Lake Constance. This application resulted in 3000 samples, which can be analyzed for up to 600 compounds yielding 1.8 million measured concentrations.

The high temporal resolution allows first for a proper quantification of peak concentration. Overall, the time-series encompassed nine rain events, during which extreme concentration peaks occurred. The fungicides fluopyram achieved 30 µg/l and cyprodinil exceeded 5 µg/l, while the herbicide napropamide reached 5 µg/l. Also during dry periods, high concentrations were observed: fungicides peaked to 2 µg/l, herbicides to 0.9 µg/l, and insecticides to 0.1 µg/l.

Yet, the temporal resolution makes it possible to investigate in great detail the PPPs dynamics during rainfall events of different characteristics yielding insights about potential PPPs sources and pathways. To that end, we compared the measured concentrations of tens of selected PPPs with meteorological observations and water level data available at 10 minutes resolution for the different events.

The high-time resolution relationships between measured concentrations and water levels of these compounds revealed interesting patterns. For the same PPP, the patterns generally differed widely across different rainfall events. For some groups of different PPPs we observed very similar patterns during the same event. However, this similarity did not always hold across different

events. This suggests that the patterns were controlled by event-specific combinations of PPPs availability and hydrological response in different parts of the catchment.

The measured concentrations-water level relationships were often hysteretic in nature. Supply limitation and transport limitation might control hysteresis. Supply limitation may refer to the lack of PPP residues in the environment; otherwise, strong adsorption can decrease PPPs availability. Transport limitation may predominate during hydrological conditions not suitable for a substantial mobilization and movement of PPPs. Comparison of different hysteresis patterns shall provide insights into the interplay between site- and event-specific mobilization of PPPs and their chemical properties leading to the understanding of how to minimize water contamination in the future.