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A Complete Analytical Screening Identifies the Real Pesticide Contamination of Surface Waters

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A comprehensive assessment of pesticides in surface waters is challenging due to the large number of potential contaminants. In Switzerland for example, roughly 500 active ingredients are registered as either plant protection agent (PPA) or as biocide. In addition, an unlimited number of transformations products (TPs) can enter or be formed in surfaced waters. Most scientific publications or regulatory monitoring authorities have implemented 15-40 pesticides in their analytics. Only a few TPs are normally included. Interpretations of the surface water quality based on these subsets remains error prone.

In the presented study, we carried out a nearly complete analytical screening covering 86% of all polar organic pesticides (from agricultural and urban sources) in Switzerland (300 substances) and 134 TPs with limits of quantification in the low ng/L range. The comprehensive pesticide screening was conducted by liquid-chromatography coupled to high-resolution tandem mass spectrometry. Five medium-sized rivers (Strahler stream order 3-4, catchment size 35-105 km2), containing high percentiles of diverse crops, orchards and urban settlements in their catchments, were sampled from March till July 2012. Nine subsequent time-proportional bi-weekly composite samples were taken in order to quantify average concentrations.

In total, 104 different active ingredients could be detected in at least one of the five rivers. Thereby, 82 substances were only registered as PPA, 20 were registered as PPA and as biocide and 2 were only registered as biocide. Within the PPAs, herbicides had the most frequent detections and the highest concentrations, followed by fungicides and insecticides. Most concentrations were found between 1 and 50 ng/L; however 31 substances (mainly herbicides) had concentrations above 100 ng/L and 3 herbicides above 1000 ng/L. It has to be noted that the measured concentrations are average concentrations over two weeks in medium sized streams and that maximum concentrations, especially in smaller streams, can be much higher. In each sample, between 30-50 pesticides were detected and the concentration sum of all active ingredients exceeded 1000 ng/L in 78% of the samples.

Forty of the 134 investigated TPs could be detected in all the five rivers. As for the active ingredients, herbicide TPs dominated the detection frequency and the concentration range. Twelve TPs exceeded 100 ng/L in at least one sample. Between 15 and 25 TPs were detected in each sample, and 35% of all samples had a concentration sum of more than 1000 ng/L.

The comparison of the measured concentrations of the parent compounds with chronic environmental quality standards (AA-EQS), revealed that 70% of all surface water samples exceeded at least one of them; in some samples up to seven AA-EQS exceedances were observed. In total, 19 substances (mainly herbicides and insecticides) exceeded critical concentrations in at least one sample.

The conducted study showed that the investigated medium-sized rivers were exposed to a large number of pesticides and TPs over the whole sampling period. For a correct assessment of the surface water quality, it is therefore crucial to measure as many pesticides as possible in order to get the real contamination of pesticides in surface waters.