Prioritizing pesticides for Swiss surface water monitoring - Theoretical selection method and analytical screening for 240 pesticides

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Introduction
Monitoring pesticides, including plant protection products and biocides, in aquatic environments is cost and time intensive. Substance lists of monitoring campaigns often consist of legacy compounds due to the historical development of such lists. Often there is a lack of knowledge on which actives are currently the most important ones. As a result, monitoring campaigns may insufficiently represent the actual pollution of pesticides in surface waters. Here, we present a combined theoretical selection and analytical screening method to select pesticides as analytes for up-to-date national monitoring campaigns. We included both plant protection agents and biocides since some compounds have a dual registration.

Method & Results
In the theoretical approach we categorized all registered and sold pesticides in Switzerland by a prioritization algorithm as either surface water relevant or irrelevant. Surface water relevance is based on whether compounds were ecotoxicologically relevant, previously measured in high concentrations, or were likely to occur in the aquatic environment. Those which were irrelevant were compounds with a half life < 1 day or which were not likely to occur in the aquatic environment. As a background for this prioritization, a pesticide surface water occurrence index was developed (only for plant protection agents) based on nationwide sales data, chemical-physical properties and soil degradation of the compound. In total, 30 out of 113 herbicides, 12 out of 80 fungicides and 15 out of 35 insecticides have been classified as surface water relevant. For the biocides such a detailed classification was difficult due to a lack of knowledge on national consumption figures and also on environmental fate.

Figure 1 The five selected catchments and their distribution in the Swiss plateau.
In the analytical approach we screened 55 two-week composite samples from five representative catchments in the Swiss Plateau (Figure 1). The size of the catchments was roughly 40km$^2$ and the catchments represented some of the highest densities of the most important national crop patterns including cereals, corn, rape seed, vineyards, fruit yards, sugar beets and vegetables and urban areas. The surface water samples were screened for all registered pesticides by high-resolution tandem mass spectrometry (LC-HRMS/MS) basically representing a full assessment of all registered compounds. From 240 pesticides (plant protection products) roughly 90 were detected at least once above the limit of quantification. From compounds registered as biocides only 22 have been found and of these 19 are also registered as plant protection products, thus the source is unclear.

Both approaches, theoretical and analytical, were in good agreement for plant protection products as compounds with a high theoretical priority were also detected above limit of quantification and vice versa. Only a few compounds, for example the insecticide thiacloprid, received a higher priority due to the analytical screening results.

The theoretical approach for biocides was less promising as for the plant protection products, mainly due to a lack of knowledge on sales data. For the selection of biocides for a future monitoring program, one would therefore have to mainly rely on the analytical approach. However, they seem to be of minor importance compared to the plant protection agents.

**Conclusion**

The newly compiled list based on both approaches can now be used for monitoring programs in Switzerland. This prioritization and selection approach should be repeated every five to ten years due to the fast changes in pesticide legislation and market developments.

**Acknowledgments**

The results are based on two projects commissioned by the Swiss federal office for the environment (FOEN). The analytical screening was part of the Swiss NAWA monitoring network.

We gratefully acknowledge the founding of the two projects by the FOEN. We gratefully acknowledge the help for the sampling by the cantons of Vaud, Zürich, Aargau, Solothurn and Thurgau. Furthermore we would like to thank Tobias Doppler for the organization and all those who helped with the analytical work namely; Alessandro Piazzoli, Jelena Simovic, Sebastian Huntscha and Philip Longree.