

Highlights of Analytical Sciences in Switzerland

Division of Analytical Sciences

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Ultrasensitive Quantification of Pyrethroid and Organophosphate Insecticides in Surface Water

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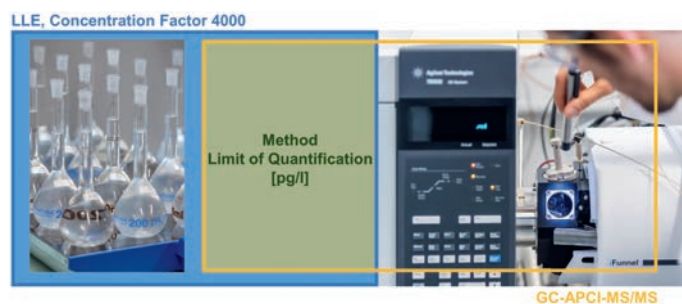
Pesticides, including herbicides, fungicides and insecticides, are frequently found in surface waters in agricultural areas, where these bioactive substances can pose a threat to the aquatic ecosystem. In particular, pyrethroid and organophosphate insecticides can be detrimental to aquatic organisms already in the pg/l range. Only recently, a quantitative analytical method able to reach these very low, but ecotoxicologically relevant concentration ranges has been developed^[1] in consultation with the Swiss intercantonal laboratory group 'Task-Force Pyrethroids'.^[2]

To determine the dissolved and particulate-bound pyrethroid and organophosphate insecticide concentrations, unfiltered water samples were extracted by liquid-liquid extraction using n-hexane up to an enrichment factor of 4000. Gas chromatography coupled to tandem mass spectrometry by means of chemical ionization under atmospheric pressure was used for ultrasensitive (pg/l) detection of these insecticides. With this approach, method limits of quantification (MLOQ) between 2.5 and 125 pg/l were achieved, thus reaching chronic environmental quality standards (AA-EQS) for pyrethroids and organophosphates for the first time. Using this method, concentrations of these insecticides were determined in six small- to mid-sized Swiss streams with agricultural land use from mid March to the beginning of October 2018. A total of 84 two-week time proportional composite samples were analyzed.

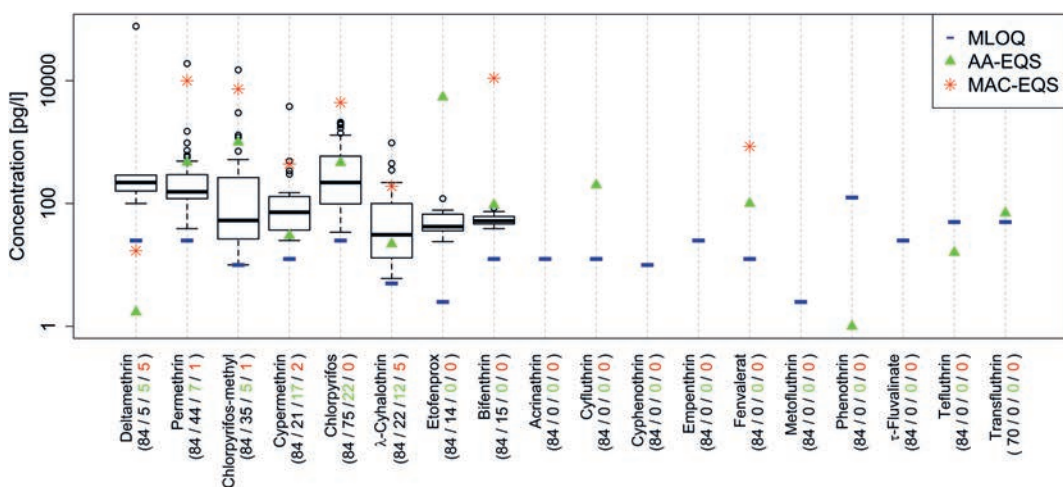
The concentrations of the individual insecticides with positive detection ranged between 6 and 77000 pg/l, with a median value of 110 pg/l. Acute environmental quality standards (MAC-EQS) were exceeded for 5 out of the 18 investigated insecticides, whereas AA-EQS were exceeded for 6 out of the 18 investigated insecticides. At least one MAC-EQS was exceeded in 15% of the samples and at least one AA-EQS was exceeded in 55% of the samples. **These results indicate at times unsatisfactory water quality in the six investigated Swiss streams, as the measured pyrethroid and organophosphate concentrations pose a risk to invertebrates, the most vulnerable aquatic organism group to these insecticides.**

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- [1] A. Rösch, B. Beck, J. Hollender, H. Singer, *Anal. Bioanal. Chem.* **2019**, *411*, 3151.
- [2] C. Moschet, *Aqua & Gas* **2019**, *99*, 2.
- [3] A. Rösch, B. Beck, J. Hollender, C. Stamm, H. Singer, T. Doppler, M. Junghans, *Aqua & Gas* **2019**, *99*, 54.



The combination of gas chromatography (GC) with chemical ionization under atmospheric pressure (APCI) and tandem mass spectrometry (MS/MS) allows for ultrasensitive quantification (pg/l) of insecticides. Photos: Alessandro della Bella, Eawag.



Concentration ranges of positively detected pyrethroid and organophosphate insecticides measured in two-week composite samples taken from six Swiss streams in 2018. The method limits of quantification (MLOQ; blue line) as well as chronic (AA-EQS; green triangle) and acute environmental quality standards (MAC-EQS; red asterisk) are indicated for each analyte. The numbers under the analyte names indicate in succession the number of composite samples analyzed (black) / number of detections (black) / number of detections > AA-EQS (green) / number of detections > MAC-EQS (red). The achieved MLOQ slightly varied between analytical runs. Here illustrated are the lowest MLOQ observed.^[3]

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