Highlights of Analytical Sciences in Switzerland

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## Detective Work on the Rhine River in Basel – Finding Pollutants and Polluters

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Around 58 million people live along the Rhine, and many are dependent upon the Rhine for drinking water and wastewater disposal. The riverside industrial activity is among the highest in the world. In order to monitor the Rhine water quality, the countries using the Rhine operate a network of monitoring stations. The first such station, the *RÜS*, was built in Weil a.R. (Germany) in 1993. This station and the associated laboratory are operated by the Agency for Environment and Energy of the Swiss canton Basel-Stadt.

Every day, the laboratory monitors over 350 substances and also performs screening of unknown compounds (non-targets). The non-target screening is based on high resolution mass spectrometry coupled with liquid chromatography (LC-HRMS/MS) detection. The LCMS data is processed by the cutting-edge, automated trend-detection software enviMass, which can recognize patterns in periodic time-series data. This software was developed in cooperation with the Eawag (Swiss Federal Institute of Aquatic Science and Technology) and it red-flags features (characterized by mass fingerprint, retention time, and signal intensity) with a suspicious temporal trend or unusually high intensities. Various compound databases (like Pubchem or Chemspider) are then queried to obtain a molecular structure. Ideally, the identification of the compound is confirmed via reference standards.
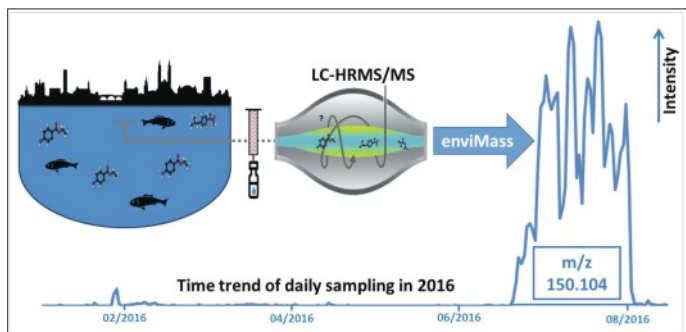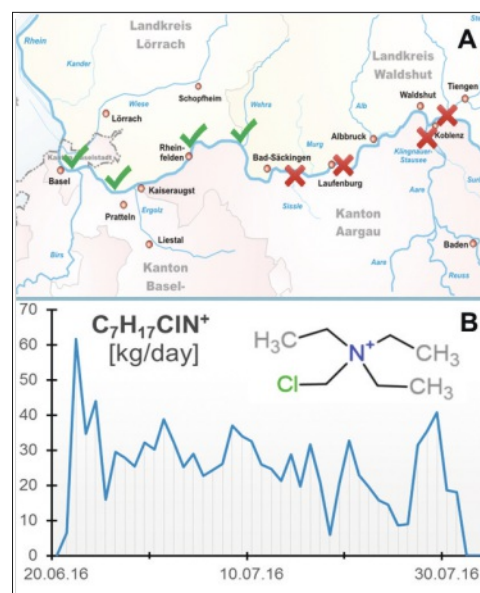
At times, the structural search is inconclusive. Additional meta information can help to identify an unknown substance. The usefulness of such complemental information can be illustrated with a feature red-flagged by enviMass in June 2016. Identification efforts suggested the structure of *N*-(chloromethyl)-triethylammonium cation, but no reference standard was available for confirmation. An upriver sampling campaign, including *e.g.* tributaries and wastewater treatment plants, revealed a point source in an adjacent canton. The company in question assisted the effort greatly by synthesizing a reference standard for the previously unknown byproduct of an industrial process. The calculated load of that byproduct into the Rhine over the period of one month was 1.1 tons. Since then the company has managed to eliminate the compound *via* process modifications.

Daily non-target-screening is essential for detecting the presence of unknown pollutants in our rivers; however, collaboration with industry and local authorities can be crucial in the enduring effort to eliminate sources of pollution and to protect our waters.

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References
J. Hollender, E. L. Schymanski, H. P. Singer, P. L. Ferguson, *Environ. Sci. Technol.* **2017**, *51*, 11505.
M. Ruff, M. S. Mueller, M. Loos, H. P. Singer, *Water Res.* **2015**, *87*, 145.
M. Loos, **2018**, *enviMass version 3.5 LC-HRMS trend detection workflow – R package*. Zenodo. *https://doi.org/10.5281/zenodo.1213098*.

enviMass is a data-mining workflow based on LC-HRMS/MS data and extraction of mass profiles in time. In June 2016, enviMass reported an unusual profile pattern of a substance with m/z 150.104 which subsequently could be identified as *N*-(chloromethyl)-triethylammonium cation.

A: Sampling sites along the Rhine with positive (green marks) and negative results (red crosses) of the substance N-(chloromethyl)-triethylammonium cation. B: Based on these findings, the source was identified and the emission stopped. The total load in the Rhine was 1.1 t.