Broadening and tightening the net

The Rhine catchment is a source of drinking water for more than 20 million people. So, given the need to detect and identify problematic substances as early as possible, it is little wonder that the Rhine is among the world's most closely monitored river systems. In cooperation with the Federal Office for the Environment and the Environment and Energy Office of Canton Basel-Stadt (AUE), Eawag is investigating how the latest analytical methods can be used to detect substances in the Rhine not previously covered by monitoring programmes.

The Weil am Rhein monitoring station, lying about a kilometre below the point where Germany, France and Switzerland meet, aims to detect possibly toxic substances at an early stage, so that waterworks can be alerted and the Rhine ecosystem protected. The substances also need to be identified so that their source can be determined and pollutant discharges controlled.

Complex measurements

Unlike water levels or temperature, the measurement of potentially hazardous substances poses complex challenges for the Rhine monitoring authorities:

▶ Measurement must allow a large number of organic pollutants to be detected, within hours if possible. Traditional analytical methods – gas chromatography coupled with mass spectrometry – cannot detect all the relevant substances, and the preparation of samples is time-consuming.

▶ Concentrations down to the low nanogram (billionth of a gram) per litre range need to be detectable. While this may appear to be insignificant, even a concentration of 10 ng/l means that a kilogram of the substance in question is flowing downstream each day.

▶ Chemical analysis primarily finds what is being sought. However, monitoring of the Rhine is also supposed to identify unexpected or unknown substances that have been released accidentally. This calls for analytical methods that can detect compounds of interest without selecting the target substances in advance.

Against this background, Eawag collaborated in 2008 with the Federal Office for the Environment to investigate the potential of an analytical method which combines liquid chromatography with high-resolution mass spectrometry. This makes it possible to determine molecular masses with an accuracy that registers the mass of a single electron.

Promising tests

The study recommended the use of this type of tandem system. Using the test system (LTQ Orbitrap), 88 % of 211 selected micropollutants were detected down to low ng/l levels with a single enrichment method. Screening of the 12 Rhine water samples yielded 672 positive findings, comprising 84 different substances, including 40 pesticides and pesticide transformation products, 26 pharmaceuticals, an anticorrosive agent and several industrial chemicals. Thanks to its resolving power, the system is in principle also capable of detecting unknown pollutants that may occur at high concentrations in the Rhine following major accidents. In combination with the technologies already installed, the new analytical method should make it almost impossible for such pollutant waves to flow undetected towards the North Sea. It could also be said that the Rhine monitoring net is being both broadened and tightened.

Continuous improvements

The researchers are still faced with one problem: with liquid chromatography, the mass spectrometry fingerprints of compounds cannot be compared directly with the existing substance databases based on standard gas chromatography. Unknown compounds have to be determined via high-accurate mass measurements. This means that a compound cannot be identified definitely, but only with a high degree of probability. The likelihood of accurate identification can be increased by predictions that narrow down the expected range of substances – if not making the needle bigger, then at least reducing the size of the haystack. Eawag is therefore currently developing prediction models to facilitate the identification of transformation products of pesticides, biocides and pharmaceuticals whose concentrations and effects make them relevant to water quality.

At the monitoring station in Weil, the AUE is now operating a liquid chromatograph coupled with a high-resolution mass spectrometer. Whether this system can wholly replace traditional analytical methods remains to be seen. For the next three years, the process is being overseen and knowledge transfer assured by an Eawag postdoc. ○○○

ETH Library, Image Archive

The Rhine port in Basel. After the devastating Sandoz chemical fire in 1986, the riparian states agreed to implement a joint Rhine monitoring programme.

Contact:
Heinz Singer, heinz.singer@eawag.ch