Protecting Our Most Precious Resource: Water

New analytical capability can have a significant impact on research direction. In environmental analysis, high-resolution accurate mass (HRAM) mass spectrometry is allowing us to explore uncharted aspects of our increasingly complex chemical world.

In conversation with Heinz Singer, Group leader of Environmental Analytical Chemistry, Eawag - Swiss Federal Institute of Aquatic Science and Technology, Switzerland (by Rich Whitworth).

I've been at the department of environmental chemistry at Eawag for 18 years, though I am very much an analytical chemist at heart. Environmental analysis demands highly sensitive and reliable methods and I love to develop such methods, so my current role is an excellent fit. My interest in analytical techniques is very much linked to the fact that I've always been a technophile – I am fascinated by the capabilities of new technology and systems. René Schwarzenbach, a professor of environmental chemistry at ETH Zurich, also set me off down the right path. I was René's first diploma student and his ambitious and motivated character was infectious.

We all know (but possibly don't often consider) that clean water is our most precious resource. At Eawag we are constantly investigating concepts and technologies that help the world deal sustainably with water bodies. Indeed, we only have one focus at Eawag: water. But many different disciplines – for example, microbiology, engineering, analytical chemistry – must work together to find solutions, which makes Eawag a fantastic place to be. The importance of water will only grow in the future; we use more water than ever before, we're living in an increasingly chemical world, and water is a great solvent.

Hot trends

Around five years ago, people used to believe that we'd learnt all we could about pesticides in water and that we didn't need to push analysis much further – it almost seemed an old-fashioned research area. But I realized that was simply not true. By their very nature, pesticides are designed to harm life in some way, which makes pesticide analysis highly relevant in water analysis – particularly in countries where regulations are less strict. Three challenges drive my interest in this area: (i) the large number of analytes, (ii) low ecotoxicological limits, and (iii) highly dynamic (rain-driven) concentration ranges.

More broadly, the screening of unknown compounds is another hot area right now. There are still unknown compounds in our water, and I don't doubt that they are important. New analytical tools are allowing us to investigate these hidden pollutants like never before.

But perhaps the hottest topic right now is contamination from industrial point sources. At the border between Switzerland and Germany there is a monitoring station, operated by the Cantonal Office of Environment and Energy Basel-City, that conducts non-targeted screening on the river Rhine using our methods and we occasionally witness huge spikes over a short period of time. Contaminants include pharmaceuticals, pesticides, and intermediates of chemical synthesis – and the load can be significant. Many researchers believed this particular problem had been solved by restrictions on industrial wastewater release, but our newfound ability to conduct non-targeted screening has proven us wrong. Evidently, we were not always looking for the right compounds of interest. We've been concentrating on risk assessments based on usage and modeling – but that is clearly not sufficient.

Monitoring industrial point source contamination is particularly challenging because it not only encompasses a huge universe of potential chemicals, but it is also dependent on time and space. Tools that allow us better coverage in terms of all aspects are therefore important.

Pesticides that are not introduced by industrial processes also exist in this complex analytical space. As noted above, concentrations in surface water are highly dependent on time (increasing with rain fall) and also location (not all areas have the same amount of agricultural land, and different crops require the use of different pesticides). This complexity – and the diverse range of pesticides in our environment – stretches our methods to the limit. Moreover, it means that choosing the right sampling technique is paramount.

What's in a sample?

There are essentially two kinds of sampling devices: passive and active. Passive sampling devices are exciting because they can perform sampling and enrichment at the site of sampling (wherever they are needed) and are easy to use. Plus, with the right kind of sorbent material, you can collect both polar and non-polar compounds. Passive sampling results in a time-weighted composite sample, but quantitation demands complex calibration because sampling rate is dependent on river flow, temperature and other factors – so they are not perfect. Active samplers, on the other hand, are more difficult to use, but are the method of choice for quantitative measurements.

Robotic sampling devices that can

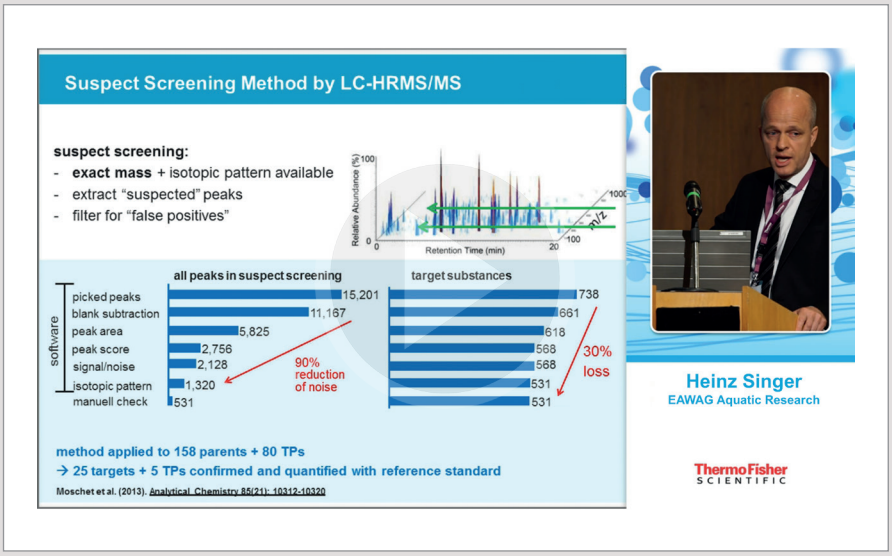
patrol areas or be remotely controlled are likely to present the future of sampling – and some research groups are already experimenting with such technology. An added advantage of remote controlled drones is that you can take horizontal or vertical profiles, which can be important in deeper water bodies, such as lakes. On-board sensors can capture other data and GPS can provide automated and exact location logging. At some point, on-board mass spectrometers would be great for continuous monitoring – but we may have to wait quite a while for that...

And though sampling is clearly important, the power of the analytical instrumentation available to us is critical.

HRAM power

Currently, we rely heavily on LC-Orbitrap™ technology with its combination of accurate mass at very high resolution. The latter is particularly important because it allows you to extract an analyte of interest from a full-scan data set. Moreover, even after measurement, if a new target analyte comes to light, you can go back to the data set and search for that compound. Such retrospective screening essentially means that the number of target analytes is unlimited. And of course, the full-scan nature of the data (with accurate mass and MS/MS information) really lends itself to our non-targeted screening approaches.

I would go as far as to say that the power of this technology has changed our field over the last ten years. We were lucky because we had one of the first Orbitrap-based systems in environmental research (in around 2006) – and the high-resolution capability has really driven our research into new directions. Of course, none of the benefits of HRAM MS would be useful without the sensitivity needed in environmental analysis – and selectivity and reliability are also key. Fortunately, Orbitrap technology ticks these boxes, which is why we have three systems in our lab.



Watch Heinz Singer's presentation at the 1st International symposium on Recent Developments in Pesticide Analysis: http://tas.txp.to/1215/Singer

The unusual suspects

Our work on screening for unexpected compounds sits somewhere between targeted analysis and non-targeted screening. Essentially, we are focusing here on compounds that we believe could end up in the water cycle (through usage data and chemical properties), but for which we might not have standards or even MS spectra available. We can create a list of suspect compounds and then search our full-scan accurate mass data set for potential matches.

Of course, the matching is not straightforward, but using software (blank subtraction, peak area/score, isotopic patterns, and so on) we can reduce the noise level in suspect peaks. In my presentation at the first International Symposium on Recent Developments in Pesticide Analysis in Prague, Czech Republic (online at http://tas.txp.to/1215/Singer) I showed how we can reduce noise by 90 percent while losing only 30 percent of our target substances. For example, we know that pharmaceuticals are used widely in huge amounts, but we only have around 130 on our target list. By assessing 1000 active ingredients using our method, we could identify a limited list of suspect peaks, 60 percent of which we were able to confirm and quantify using reference standards. The result? Thirty or so pharmaceuticals that have never been detected before; some were brand-new blockbuster drugs and others were from manufacturing point sources. In fact, we were surprised to identify drugs that are not even registered for use in Switzerland because they were actually being produced for the global rather than local market.

Addressing blind spots

Environmental monitoring programs are somewhat limited by the fact that we are typically looking for compounds that have been detected by previous monitoring campaigns, and I believe this self-evaluating cycle has created many blind spots. But new technology can increase our scope. For example, increased sensitivity allows us to investigate insecticides, which although not used in large quantities are highly toxic.

Certainly, at Eawag we are always on the look out for new technology that increases our analytical capability – there is no single system that can satisfy all our current and future analytical needs. To that end, it's important to work with a constantly updated toolbox, selecting the best tools for the analytical task at hand.

I strongly believe that fully understanding and embracing new technology can shape our research and allow us to move into previously uncharted territory – and that is the most exciting place to be!

Raising the Bar for Routine Analysis

The Pesticide Explorer Collection comprises four complete workflows that meet the challenges of modern pesticide residue analysis. High-resolution, accurate mass measurements – courtesy of Orbitrap™ technology – represent the ultimate solutions for laboratories that want to take routine analysis to the next level.

We previously introduced the Pesticide Explorer Collection and shared details of the "Standard Quantitation" (see tas.txp.to/1215/standardquan) and "Premium Quantitation" packages (see tas.txp.to/1215/premiumquan). In the final article, we introduce the "HRAM Quantitation" and "HRAM Screening and Quantitation" solutions, both of which benefit from the analytical power of the Thermo Scientific™ Q Exactive™ Focus MS system.

Definitive quantitation

The Orbitrap-based "HRAM Quantitation" configuration uses the Thermo Scientific UltiMate™ 3000 LC system as the separation platform – as do all Pesticide Explorer Collection solutions – but differentiates itself with high-resolution, accurate mass analysis – a unique capability that enables quantitation without compromise in sensitivity, accuracy, precision, and linear dynamic range. When it comes to the complex matrices often encountered in food analysis, high resolving power is particularly useful because it overcomes the masking effects of isobaric interferences, allowing detection of pesticides at very low concentrations.

As with all packages of the Pesticide Explorer Collection, HRAM Quantitation comes with all the workflow components needed, from consumables (including the QuEChERS sample preparation reagent kit and HPLC columns), essential hardware and software. The complete package facilitates method development and ultimately enables fast, accurate and cost effective routine pesticide determinations.. Indeed, pre-configured instrument methods for targeted quantitation enable you to start acquiring data with a lot less time and effort – one of the main focal points during development of the collection, according to Dipankar Ghosh, Global Director for Environmental, Food Safety & Industrial Markets at Thermo Fisher Scientific.

When it comes to data analysis, the addition of the HRAM Spectral Fragmentation Library (fully integrated and searchable using TraceFinder™ software) – with over 2,600 compounds and more than 15,000 spectra – gives you the ability to identify compounds with speed and confidence.

Adding non-targeted screening to the mix

The high-resolution accurate-mass MS/MS spectral library is also key for "HRAM Screening and Quantitation" as it also facilitates screening of non-targeted compounds. But in the ultimate Pesticide Explorer package, it is joined by two other powerful pieces of software: Thermo Scientific Compound Discoverer™ and SIEVE™. Compound Discoverer includes an extensive set of tools to ensure confident compound identification and structural elucidation. And SIEVE enables label-free, semi-quantitative differential analysis of complex LC-MS datasets, allowing you to reproducibly identify components with statistically significant inter-sample differences.

Naturally, it's not all about the software; the HRAM Screening and Quantitation package also fully exploits the power of the Q Exactive Focus system, which allows targeted quantitation and non-targeted screening from a single dataset. With MS/MS HRAM analysis, no sample-specific method optimization is necessary, and the risk of missing important non-targeted compounds is greatly reduced. Once the data has been acquired, it can be reanalyzed retrospectively without the need for sample reinjection.

Ghosh notes the upcoming nature of non-targeted methods, "Though our triple quadrupole MS-based solutions excel in targeted pesticide analysis, the Q Exactive Focus unlocks the door to unknown screening in routine environments, using the power of Orbitrap technology. This is of increasing importance given the globalized nature of the food industry. And, of course, this capability extends well beyond pesticides."

And as Kate Mastovska stated in a recent article on the never-ending challenges of pesticide analysis (visit http://tas.txp.to/1215/Mastovska), "When we consider our ever-expanding list of compounds in our target list (right now, we are currently validating a method that looks at over 500 compounds), the ability of HRAM-MS systems to perform non-targeted analysis starts to look increasingly attractive."

For more information on the Pesticide Explorer Collection, visit: http://tas.txp.to/1215/explorer