EMERGING CHEMICAL CONTAMINANTS: WATER ANALYSIS MOVES UP A GEAR

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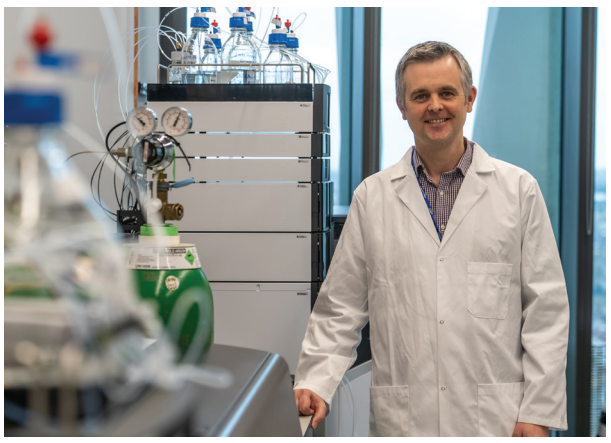


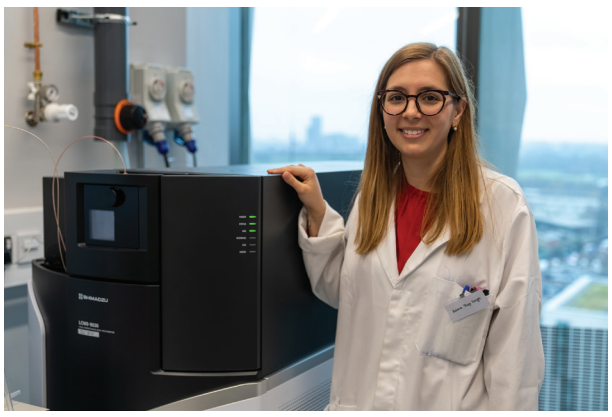
Dr Leon Barron

Understanding the environmental burden of chemical pollutants

Dr Leon Barron has had a lifelong passion for analytical chemistry – and in his current role at Imperial College London, he's using his experience to help understand the effect that humans are having on the environment. "We're looking to chemically profile water in unprecedented detail – including not just regulated chemicals on target lists, but to get a handle on everything that's in the water, especially unregulated chemicals and those we know very little about", he says. "All this is part of a drive to put a figure on how much these chemicals are contributing to the environmental burden of pollution, and by how much we're exceeding the 'planetary boundary' for so-called 'novel entities', as defined by a team at Stockholm University back in 2009".

Dr Barron leads the Emerging Chemical Contaminants team at Imperial, which is one of nine teams forming the Environmental Research Group, itself part of the School of Public Health. This is a leading provider of air and water quality information in the UK, and uses a range of approaches to determine the impacts of pollution, as well as supporting actions to mitigate those effects.

As it happens, Dr Barron didn't so much join a team at Imperial, as create one from scratch. "We got a great opportunity to build a new research group with a particular focus on chemical pollution: we've basically designed a new home in a brand-new building at Imperial's White City campus, including the offices and labs, then worked out what equipment we needed to future-proof our capability, and staffed it too".



Dr Helena Rapp Wright

One of those staff members is **Dr Helena Rapp Wright,** who arrived in 2021, and is now settled in as one of 12 team members in the Barron lab. She is one of the main users of the group's Shimadzu LCMS equipment for analysis of organic chemicals in water, which is focused on so-called 'chemicals of emerging concern' – unregulated metabolites and transformation products that have been detected in the environment. As Dr Rapp Wright explains, "New chemicals are constantly being registered for use, but in addition to these, there are tens or even hundreds of thousands of unregulated metabolites and transformation products that have been detected in the environment. The problem is that we simply don't know very much about these chemicals – and because of the sheer number of them, we need really powerful tools to separate, identify, and quantify them".

Maximizing sensitivity, robustness, and speed

This is where the Shimadzu instrumentation comes in, says Dr Barron: "We have two LCMS-8060 systems, which we use for our routine target analyses and target research, and also we've recently acquired an LCMS-9030, which we're using largely for suspect screening". He goes on to say how their systems deal with the challenges posed by their samples: "To achieve our research goals, we need sensitivity, robustness, and speed. And what's great for us is that our 8060 and 9030 systems do brilliantly on all three".

"On the sensitivity front, on both the 8060 and 9030 we can routinely get down to low nanograms per litre levels, equivalent to low ppt, which is vital for picking up on those really trace-level substances. This means we now routinely directly analyze only 10 µL of a filtered sample". He adds that robustness is another big issue for the team, because they wanted to inject raw municipal wastewater, without any form of cleanup other than filtration: "Most analysts would be horrified by that – but thanks to Shimadzu's help with method setup, we've been doing it for nearly three years now… and we still have the same instruments!".

But overall the most important thing for the team's research capability is speed, with the LCMS-8060 system using run times of just over 5 minutes, translating to about 260 injections per day. Dr Barron explains what this means for the team's research: "Once you've factored-in quantitation in triplicate for 200 chemicals, plus matrix-matched calibration lines, we can deal with between 30 and 60 samples a day. This allows us to take lots of samples across a geographical area or a time period, and so get really fine-grained information on the distribution of the chemicals we're seeing".

The team's 9030 system has been running since October 2021, and has allowed them to extend the number of chemicals that they can detect, he adds: "Because it's a QTOF, it's got the high-resolution mass capability needed for suspect screening. Currently we're looking at about 1200 compounds – and in a run time of about 17 minutes!".

Easy data-processing and reliable technical support

All this gives the team a vast quantity of information, so ease of data processing is really important for them. Dr Rapp Wright uses the systems daily, and says numerous features of the software help to streamline her work – from the easy-to-understand graphs, to the flagging system in the data explorer. Also crucial to the work on the 9030 is the MS compound library focused on pharmaceuticals and pesticides, and which was created with the help of Shimadzu experts.

Having a seamless data flow between the instruments is also vital for their work, she says: "They're actually really interdependent on each other – so for example, we often use the 8060 as a quick

way to identify a point source of pollution, or ingress of a chemical into an aquatic system. And then we run the 9030 to find out what else is there, and then some of those chemicals might be flagged up for quantitative monitoring back on the 8060".

And through the whole process – from lab configuration to method design and ongoing support – the Shimadzu team have been there, ready to help them at a moment's notice. Dr Barron says: "In our research, we've got to deliver a large number of sample analyses, so we've got to keep our instruments running pretty much 24/7. Where I've been particularly impressed with Shimadzu is the quality of their support, even during the pandemic. The overall responsiveness of the team all the way through has been brilliant".

Reimagining achievable results with LCMS

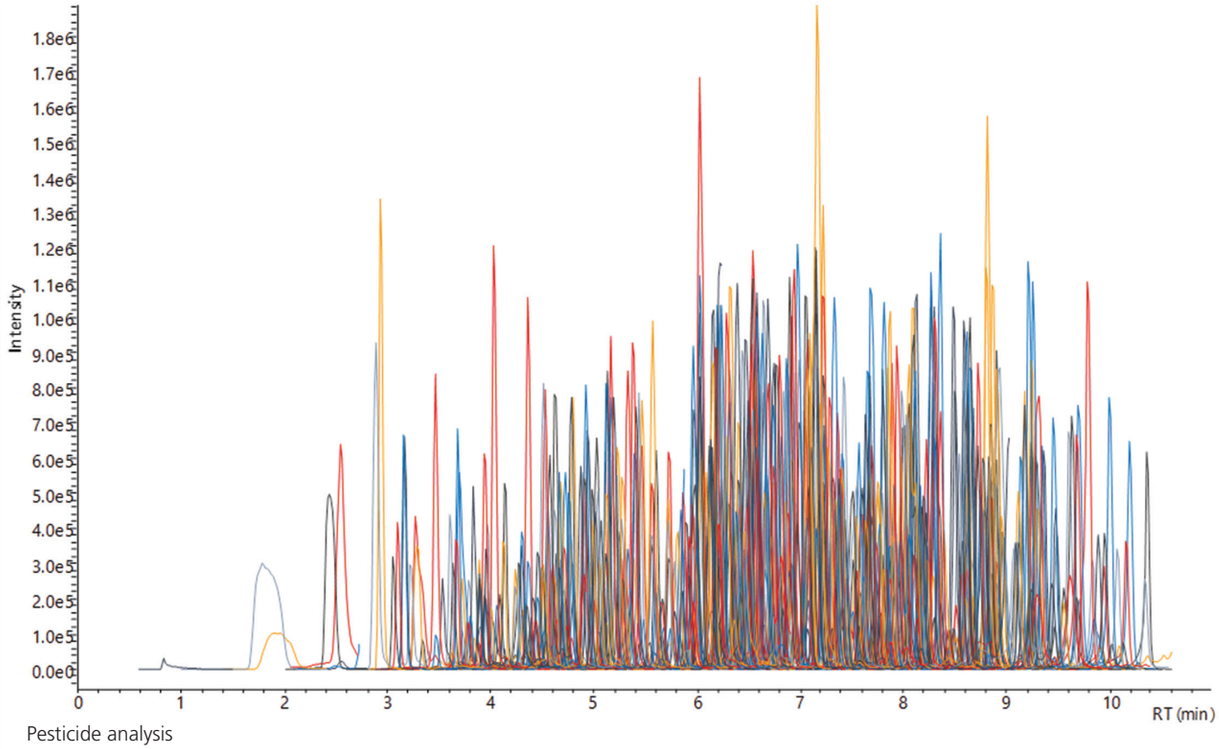
So what about their results? Dr Barron is keen to highlight the significance of what they've done: "We've absolutely slashed the run time and sample volume for this sort of analysis, which has allowed us to achieve the sample throughput needed for large-scale monitoring projects. For example, in some recent work, we monitored over 100 sampling sites on the River Thames, for over 200 chemicals of emerging concern every time, with all the samples and data analyzed on the 8060 to provide a risk assessment within a month. If you'd asked me a few years ago, I'd have said this wasn't possible!".

And the data is great quality too, says Dr Rapp Wright: "Because we're injecting the raw sample, we're not losing analytes from our samples during the extraction process – so our calibration lines on our 8060 quant work are perfectly straight in most cases, with R2 values that are absolutely spot-on!".

This analysis of 652 pesticides on a Shimadzu LCMS-8060 in just over 10 minutes is a good example of the performance that can be routinely achieved in the Barron lab. The method used (see L.P. Barron and N.J. Loftus, Chromatography Today, August/September 2019) is also applicable to suspect screening on the LCMS-9030.

Pushing the boundaries of suspect screening

The team has also been working on integrating machine learning into the analytics workflow, helping them to streamline compound matching using not just the mass spectra, but also the chromatography. "One ongoing project is to use machine learning to predict retention times for unknown compounds



Pesticide analysis

using a variety of LC modes, and by feeding that data into the compound-matching algorithm, we can reduce the list of potential matches by two-thirds, and so prioritize the reference materials we need to source".

Such methods, he says, could dramatically change the range of compounds that could be routinely monitored: "Currently we can do about 1200 chemicals for our suspect screening, but ideally we'd like to add a zero or two to that number, to take account of transformation products, metabolites, and so on – and our Shimadzu equipment in conjunction with machine learning might just enable us to do that".

LCMS: An essential tool for tackling emerging chemical contaminants

Taking a broader perspective on the team's work, it's clear that demand for this combination of subject expertise and analytical performance will continue to increase. Dr Barron summarizes the state of play: "The issue of emerging chemical contaminants isn't going away, so I think we'll see a growing need for highly-resolved watercourse monitoring, working out routes of exposure, understanding the role of synergetic effects between chemicals, and much more besides".

Until very recently, such capabilities would have seemed impossible to achieve, but Dr Barron makes it clear that this has changed: "Our Shimadzu 8060 and 9030 systems are now an essential part of our toolkit for achieving high-speed, high-sensitivity analysis. In this way, we're helping to obtain a fuller picture of chemical pollutants, and so helping to reduce humanity's footprint on the environment. This whole area is on course to receive a lot more attention in the coming months and years, especially given the current proposals to create a UN science body for chemical pollution, modelled on those for climate and biodiversity".

And throughout all their work, they've been able to rely on Shimadzu's support, says Dr Barron: "They've always been keen to understand emerging challenges, refine instrument setups, and develop new methods; and for me that's what sets them apart from other manufacturers. We wouldn't have achieved the results we've got without their enthusiasm and hard work, that's for sure!".

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