WHAT'S NEW IN THE ANALYSIS OF COMPLEX ENVIRONMENTAL MATRICES?

This was the question posed at a meeting held in the Royal Society of Chemistry (RSC) Burlington House headquarters in London in March. The one day conference was organised jointly by the Environmental Chemistry Group, the Water Science Forum and the Separation Science Group of the RSC and covered a wide range of topics of interest to those interested in the application and practice of environmental analysis. This brief report highlights some of the interesting themes and the relevant topics presented by leading scientists in their field.

Dr Leon Barron describes the analytical protocols he has developed to screen drugs in waste water

Prof Jacob De Boer discusses the rise in brominated flame retardants in the marine environment

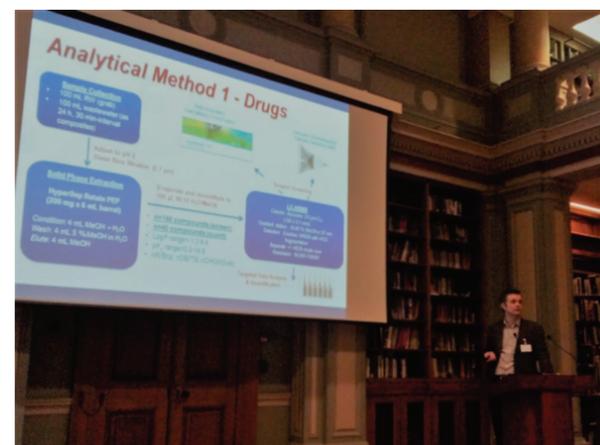*Pictures (Courtesy of Dr Roger Reeve, RSC Environmental Chemistry Group)*

Waste Water Analysis and Profiling

Dr Leon Barron from Kings College London gave a very engaging presentation on the screening of complex forensic and environmental samples using high resolution analysis and *in-silico* data mining tools. He described the screening of waste water entering London's sewage treatment works using liquid chromatography coupled with high resolution mass spectrometry (LC- HRMS) for pharmaceutical residues, drugs of abuse and compounds indicative of clandestine explosive manufacture. The use of HRMS produces large volumes of data rich in isotopic and structural information but analysis of the data can be difficult. Dr Barron and his co-workers have developed *in-silico* data mining, including retention time models using artificial neural networks (1) and machine learning, to facilitate the analysis of these large data sets. He also described the application of the techniques for the community-wide estimation of drug and pharmaceuticals consumption in England using wastewater analysis for a large number of compounds including stimulants, hallucinogens and their metabolites, opioids, morphine derivatives, benzodiazepines, and anti-depressants.
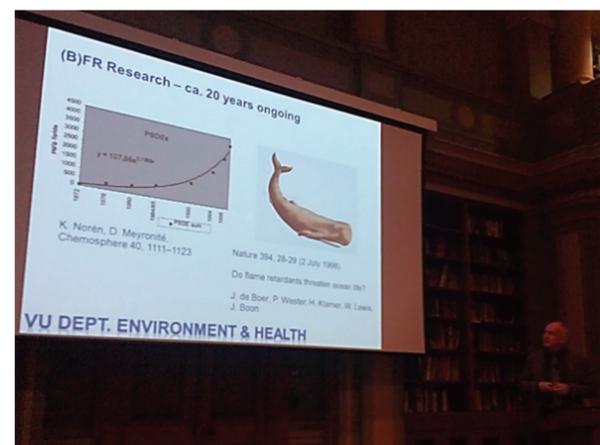
Dr Barron also described a very interesting application of SPE pre-concentration with LC-HRMS of a range of organic explosives in London's waste water in an attempt to identify illicit explosive manufacturing activities.

Waste water analysis was also covered by Erika Castrignanò, from Professor Barbara Kasprzyk-Hordern's Environmental Chemistry Group at the University of Bath UK, who described their work developing urban water analysis techniques for the profiling of community wide health and lifestyle trends. Metabolites of compounds of interest which were present at detectable levels and had good stability were targeted, including specific biomarkers for cocaine use, and the results were used to generate the health and lifestyle profiles. The group also employed enantioselective analysis and ratio comparison to give valuable insights into legal and illicit drugs use e.g. by tracking the S+R isomeric ratio of amphetamine in waste water they could monitor the use of both prescribed and illicit drugs. The technique was also employed to monitor MDMA (ecstasy) in waste water as one isomer is metabolised and the other is not - thus determining the enantiomeric ratios allowed the researchers to track whether the drugs had resulted from human consumption or direct disposal into the waste water system. Many metabolites of interest are also enantiomeric and tracking their concentrations can therefore be employed to generate insight into community wide health and lifestyle trends.

Luigi Lopardo from the same group went on to describe the applications of these techniques to study community-wide exposure routes and risks from environmental endocrine disrupting chemicals.

Fire Retardants in the Environment

Both Prof Jacob De Boer (Vrije Universiteit Amsterdam, Netherlands) and Prof Stuart Harrad (University of Birmingham, UK) discussed the increasing concerns around the rising levels of fire retardant chemicals in the environment and especially indoors in the home and workplace. Professor Harrad introduced brominated fire retardants and described how they added to a wide range of products to make the them more fire resistant by slowing the burning process. For example, in many plastic components, such as the carcasses of TVs, PCs, phones, games consoles and tablets, the levels can be as high as 30% and in furniture typically 2-3%, and this has resulted in high levels being detected in the household environment and therefore significantly increasing human exposure to these chemicals. He described how the levels of PolyBrominated DiEthers (PBDE) detected in human milk has been doubling every 5 years and this together with increasing levels in household dust etc. has led to increasing concern for the effects of these chemicals on health. A major area of concern was the growing levels of electronic waste (circa 20m tonnes pa) containing high levels of these compounds and how it is processed and recycled. He described how levels of Hexabromocyclododecane in air at an e-waste centre was 400 times higher than the background.

In the developed countries increasing awareness of the issues was being addressed by legislation but in developing countries e-waste control was not widespread and this was a major problem for exposed workers, the food chain and the wider environment. He described his work studying levels found in animals from the food chain near e-waste sites in China (2). High-end estimates of exposure for young children eating these foods exceeded the U.S. Environmental Protection Agency reference doses for BDE-47 and BDE-99 by factors of approximately 2.5 and 1.5, respectively.

Although e-waste is now largely separated from waste before landfill there is still a legacy issue and Prof Harrad described the development of leaching experiments under landfill conditions where they observed high leachate concentrations especially from textile based wastes. TCPP (tris (1-chloro-2-propyl) phosphate) is a flame retardant, commonly used in polyurethane foam in consumer products and home insulation, and in experiments which mimicked rainfall leaching cycles the team found that almost all (96%) had been leached after only 6 cycles thus raising concerns for possible contamination of the water table.

Another area of concern was that they are now finding increasing levels of flame retardants in items which do not need fire retardancy, for example in cooking utensils with black plastic components, due to the increasing use of recycled plastics

Prof Jacob De Boer in his Keynote lecture described the application of Direct Probe - ACPI(+)-TOF-MS to screen for brominated flame retardants (BFR) present at high levels in a range of sample matrices. Using this technique, a sample can be screened every 2 minutes for a selected target compounds. A comparison of BFRs found in sewage sludge in the UK and the Netherlands showed

much higher levels in the UK samples which was attributed to the UK having stricter legislation forcing the inclusion of fire retardants in furniture and textiles and they also found much higher concentrations in areas with significant textile industries. Prof De Boer also discussed the work of ENFIRO which is a European Commission-funded project to offer a prototypical case study on substitution options for specific brominated flame retardants and the move to newer halogen free phosphorus based retardants.

The direct probe technique was also reported to be suitable for the screening of other chemicals of interest such as Bis Phenol A and its alternatives.

Prof De Boer then moved on to Chlorinated Paraffins where a global ban on Short Chain Chlorinated Paraffins (SCCP) is being considered under the Stockholm Convention on Persistent Organic Pollutants. He described the application of 2D Gas Chromatography with Electron Capture Negative Ion Mass Spectrometry (GCxGC -ECNI-MS) to gain greater resolution of the degree of chlorination in these chemicals.

It was clear from both presenters that much higher levels of these compounds are now being found indoors rather than in the outside environment, especially in the dust in the home and in cars and as a result of increased plastic recycling in products intended for use by babies and children.

Environmental Technique Developments

Prof Colin Creaser (Loughborough University, UK) gave a presentation highlighting the potential benefits of coupling ion mobility spectrometry with mass spectrometry for environmental applications and especially for the pre-separation of isobaric and isomeric compounds prior to entering the mass spectrometer.

Mark Perkins (Anatune, UK) gave a presentation on VOC measurements in ambient air using the unique features of Selected Ion Flow Tube Mass Spectrometry (SIFT)-MS and focussing on the automation and calibration aspects of this relatively new technique.

Andrew Sweetman (Lancaster University, UK) described the use of passive samplers as a potential compliance tool within the EU Water Framework Directive.

Gavin Mills (Severn Trent Ltd., UK) gave a presentation describing how water companies investigate taste and odour issues in drinking water. In addition to human panels to taste and smell the samples pre-concentration techniques such as SPE and Stir Bar Sorptive Extraction (SBSE) are employed prior to GC-QTOF-MS and olfactory analysis to identify the source of the taints and odours.

The Norman Network

Prof Jaroslav Slobodnik from the Environmental Institute in the Slovak Republic gave a fascinating keynote lecture titled "Non-target screening of environmental pollutants in the context of risk assessment of European river basins: the NORMAN network perspective". The NORMAN Network is an EU funded network of reference laboratories, research centres and related organisations for the monitoring of emerging environmental substances. The scope of this network and activities is vast and we could not do it justice in this brief report but we hope to bring you a more detailed description of the activities in a future article. Readers interested in following its activities are recommended to visit http://www.norman-network.net/ .

Overall this was a fascinating and absorbing one day meeting with top class presentations from recognised experts in their fields and compliments must go to the RSC Groups organising committee for putting together such a topical and well balanced programme.

References.

(1) Artificial neural network modelling of pharmaceutical residue retention times in wastewater extracts using gradient liquid chromatography-high resolution mass spectrometry data.
Munro K, Miller TH, Martins CPB, Edge AM, Cowan DA, Barron LP, Journal of Chromatography A, 2015, 1396, pp 34-44

(2) Human Dietary Exposure to PBDEs Around E-Waste Recycling Sites in Eastern China. Labunska I, Harrad S, Wang M, Santillo D, Johnston P, Environ. Sci. Technol., 2014, 48 (10), pp 5555–5564

(3) Organophosphorus flame retardants (PFRs) and plasticizers in house and car dust and the influence of electronic equipment. Brandsma SH, de Boer J, van Velzen MJM, Leonards PEG, Chemosphere, 2014 Dec, 116, pp 3-9

What's new in the analysis of complex environmental matrices?

Royal Society of Chemistry
Environmental Chemistry Group, Water Science Forum and the Separation Science Group Joint Meeting

Friday 3rd March 2017
at
Science Suite, Royal Society of Chemistry, Burlington House, Piccadilly, LONDON, W1J 0BA

9.00-9.40 am Registration and coffee

9.40-9.45 am Graham Mills (University of Portsmouth, UK)
Opening and welcome to meeting

9.45-10.15 am Leon Barron (King's College London, UK)
Screening of complex forensic and environmental samples using high resolution analysis and in silico data mining tools

10.15-10.45 am Andrew Sweetman (Lancaster University, UK)
Use of passive samplers as a potential compliance tool within the EU Water Framework Directive

10.45-11.15 am Coffee break

11.15-11.45 am Colin Creaser (Loughborough University, UK)
Combining ion mobility spectrometry with mass spectrometry for the analysis of complex samples: the potential for environmental analysis

11.45-12.15 pm Stuart Harrad (University of Birmingham, UK)
Brominated flame retardants in waste consumer articles

12.15-1.00 pm (Keynote Lecture) Jaroslav Slobodnik (Environmental Institute, Slovak Republic)
Non-target screening of environmental pollutants in the context of risk assessment of European river basins: the NORMAN network perspective

1.00-2.15 pm Lunch break and vendors' exhibition

2.15-3.00 pm (Keynote Lecture) Jacob de Boer (Vrije Universiteit Amsterdam, Netherlands)
Human exposure to environmental contaminants: direct probe time-of-flight mass spectrometry reveals a multitude of chemicals indoors

3.00-3.30 pm Gavin Mills (Severn Trent Ltd., UK)
Advances in the determination of taste and odour compounds in drinking water

3.30-4.00 pm Barbara Kasprzyk-Hordern (University of Bath, UK)
How can urban water profiling inform our understanding of the state of the environment and public health?

4.00-4.30 pm Mark Perkins (Anatune, UK)
VOC measurements in ambient air using Selected Ion Flow Tube Mass Spectrometry (SIFT)-MS - automation and calibration considerations

4.30 pm Roger Reeve (University of Sunderland, UK)
Meeting close

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