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Conference Call

Chemistry and the Environment

by Diane Purchase, Sherine Obare, John Unsworth and Hemda Garelick

The IUPAC 46th World Chemistry Congress (in Sao Paulo, Brazil, 9-14 July, 2017) emphasized the importance of the link between chemistry and the environment in their 'Energy, Water and Environmental Science' programme. The Chemistry and the Environment Division of IUPAC (Division VI) has sponsored and organized three symposia to present the latest advances concerning the environmental impact of emerging technologies and the fate of pollutants in the environment. Additional financial support was provided by the IUPAC Project Committee under the 'New Directions in Chemistry' initiative.

The symposia took place over two days (11-12 July 2017), a number of high-profile international speakers presented on:

- E-waste—an emerging global environmental challenge
- Global Environmental Challenges of Nanomaterials
- Fate of Pesticides in Latin American Environments

All three symposia were well-attended and well-received, raising awareness of the three important topics associated with the work and expertise of Division VI membership. They also provided the opportunity to address specific regional problems and expand current, mainly EU and US based networks.

E-waste—an Emerging Global Environmental Challenge (coordinated by Diane Purchase)

The waste stream of obsolete electronic equipment grows exponentially, creating a worldwide pollution



problem. E-waste contains potential contaminants that are distinct from other types of waste. The e-waste stream comprises a mixture of different metals, metalloids, glass, plastics, flame retardants and valuable materials such as gold, silver, copper and aluminium. They cause considerable environmental and health impacts and pose substantial challenges in waste management. This symposium highlighted the challenges and opportunities in tackling this emerging, global, environmental concern.

Our keynote speaker, Professor Christer Forsgren, is the Technical and Environmental Director of Stena Recycling International as well as the Adjunct Professor in Chalmers Technical University Gothenburg, Sweden. Stena Recycling International (SRI) is a part of the Stena Metall Group, a family owned company active mainly in the northern part of Europe on about 200 sites. Annual turnover is about 2 billion US\$. Professor Forsgren provided a valuable industrial perspective of the formal treatment of electronic waste. His presentation outlined the different, state-of-the-art technologies for the recovery of precious metals, separation of brominated and non-brominated plastics and the recycling of Li-ion batteries. He also explored the concept 'Design for Complete Lifecycle' that can help to reduce the in-use energy consumption of devices, improve the efficient use of resources



Technology	Possibility	Limitation
Density	Enrichment, BFR/non BFR	Unspecific, high diver
NIR	Rep polymer type, Ind available	Not for black plastics
Electrostatic	ABS from PS	Mixture limitations
WRT	BFR/non BFR	No sorting of polym
Handheld SSI/MIR	Separation of polymer type	Not automatic or BFR
Ultrasonic	Sorting polymer type, black parts possible	Not for BFR/Non BFR
XRF, LIBS, etc	Separation BFR/Non BFR	Non state of art

Top: Dr Oluseun Popoola, Above: Professor Christer Forsgren, Left: Professor Ming Hung Wong

in their manufacture and increase the possibility of product/component reuse and repair.

A keenly contrasting e-waste experience was provided by Dr Oluseun Popoola from Yaba College of Technology, Nigeria. Dr Popoola has for a number of years, carried out research on the health of the workers in an informal recycling site in Nigeria. She catalogued the challenges facing developing countries: illegal shipment, weak environmental regulations, paucity of technology and inadequate waste treatment structure. Her research showed that biological samples from the workers contained high levels of toxic metals resulting from the crude recycling process—often involving direct burning of the waste. Even though the subjects are aware of the health impacts, they continue to be involved in the informal recycling of e-waste due to intense social and economic deprivation.

On the other side of the globe, China has one of the world's mega sites for uncontrolled recycling of e-waste, with end-of-life electronic and electrical products shipped from the more affluent countries. Professor Ming Hung Wong from the Education University

in Hong Kong is the Regional Coordinator of Central and North-East Asia of the project “Regionally Based Assessment of Persistent Toxic Substances” sponsored by United Nations Environment Program (UNEP) and Global Environment Facility (GEF). Professor Wong is also a panel member to review a UNEP/GEF initiative “Emerging Chemicals Management Issues in Developing Countries and Countries with Economies in Transition” with the aim of understanding the sources and preventing adverse impacts of chemicals on human health and the environment in rapidly developing countries. In his presentation, Professor Wong reviewed the sources, fates and environmental effects of toxic chemicals due to e-waste processing in Guiyu, Taizhou and Hong Kong. He presented a critical evaluation of the e-waste management systems in China in the past decade and the lessons learnt. He also charted some of the progress made by the Chinese government to tackle the e-waste problem as well as offered additional recommendations for further improvement.

Clearly, such a global challenge can only be managed via interdisciplinary collaborative efforts. Dr Bradley Miller from the US EPA elaborated upon the management of e-waste in the US and to identify opportunities for improvement, good practices to be shared and also pitfalls to be avoided. He provided information on the National Strategy for Electronics Stewardship which details the federal government's plan try and reduce e-waste by incentivizing the production of “green” electronics; mandates that the federal government purchases “green” products, increasing domestic recycling, and reducing exports of e-waste. At the national level, some e-waste is regulated under the Resource Conservation and Recovery Act (RCRA), which identifies and regulates hazardous waste in the US. Individual states take the lead in management of non-hazardous waste, which includes household waste, where most e-waste is regulated.

Dr Kirankumar Surati of Sardar Patel University, India, presented his research on organic, bio-degradable semiconductors that could open new avenue in addressing the challenge at the point of manufacturing by using sustainable alternative materials. He presented a number of organic biodegradable compounds that can easily degrade and are useful for fabricate advance organic semiconductor devices. He suggested that such device and materials were one of the best ways to minimize the e-waste. He argued that the organic biodegradable molecules were superior in terms of cost, environmental friendly and easy processability with respect to presently use materials (such as cobalt, gallium, germanium, indium, platinum group metals,



Top: Dr Bradley Miller, Above: Dr Kirankumar Surati—
Biodegradable materials for semiconductors

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rare earths. He also indicated that these energy efficiencies of bio degradable organic semiconductor is higher with respect to conventional semiconductor materials.

Last, but not least, Professor Rafael Luque of Universidad de Cordoba, Spain, discussed a couple of newly-patented technologies for e-waste valorization to obtain valuable products (materials, chemicals, etc.) that can also facilitate future recycling and/or management of e-waste and provide alternatives towards a more sustainable valorisation and subsequent management.

Global Environmental Challenges of Nanomaterials (coordinated by Sherine Obare)

The overall objective of the symposium was to assess the current framework for understanding the environmental health and safety of nanoparticles (NPs). With an increase in the manufacture and use of NPs in consumer products, there continues to be a needed international consensus on their design, analysis, and determination of their environmental and health impact. The growth in manufacturing and use of anthropogenic NPs will lead to their presence in the environment. The interactions of the NPs with the environment will depend highly on their chemical composition, size, shape, morphology, surface coatings, environmental pH, and ionic strength. All these parameters play an important role on the chemical speciation of the NPs and consequently their toxicology and ecological risk assessment. In order to obtain a molecular level understanding of the materials speciation and consequently transformation, a group of experts consisting of chemists and environmental scientists came together for a symposium held at the 2017 IUPAC Congress in Sao Paulo, Brazil, to discuss critical issues in the chemistry of NPs.

Professor Sherine O. Obare from Western Michigan University gave a talk titled “*Assessing the environmental impact of anthropogenic nanoparticles*,” focused on anthropogenic NPs that have gained increased usage in industrial processes as well as in commercial products. The presentation discussed some of the critical issues that arise in understanding the environmental health and safety concerns of nanoparticles, including the method of preparation, and the resulting properties. In order to obtain a molecular level understanding of the materials speciation and consequently transformation, it is necessary to develop well-defined and well-characterized nanoparticles. Several synthetic protocols were discussed that showed the difference

in results obtained when using well-defined materials versus when using commercial materials that lacked uniformity. Consequently, well-defined nanoparticles were used to conduct studies to assess the toxicity of the nanoparticles and correlate the results specifically to the particle size, shape and composition. The results showed that relationship between nanoparticle morphology, their transformation in the environment and their impact on biological species. The interaction of nanoparticles with various environmental components and the analytical methods required for their assessment were also described and showed a systematic method that leads to a critical understanding of the toxicity, bioavailability, and environmental fate and transport of nanoparticles.

Professor Rafael Luque from Departamento de química Organica, Universidad de Cordoba, gave a talk titled “*Addressing nanomaterials toxicity: benign-by-design protocols towards biocompatible nanomaterials*.” The presentation focused on the increasing appreciation of the functionality and complexity of such systems that has prompted researchers to consider a number of fundamental properties (e.g. mechanical and biological compatibility, corrosion resistance in biological environments, etc.) and to address important issues such as their speciation and potential environmental impacts. The talk provided case studies of benign-by-design nanomaterials that have been characterized and addressed in terms of cytotoxicity and environmental impacts, exhibiting improved properties as compared to commercial analogous nanomaterials.

Professor Anna Cristina S. Samia from the Department of Chemistry at Case Western Reserve University, gave a keynote address titled “*Effects of metal oxide nanoparticle exposure on plant growth and on the*



Left: Professor Rafael Luque, Right: Professor Anna Cristina S. Samia

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local soil microbe population,” that focused on metal oxide NPs, a class of materials with increased use in commercial applications. Despite their growing applications, little is known about their long-term effects on plants and their fate in the environment. Recent reports have indicated both negative and positive effects of different types of nanoparticles on plants in terms of their growth and seed germination. Several factors have been shown to influence the plant-nanoparticle interactions, including plant type, growth media, as well as the nanoparticle concentration, size, composition, and surface chemistry. To date, there is still no conclusive explanation and definite mechanism on the toxicity of nanoparticles in plants, particularly in the soil environment, and further studies are needed to explore their effects in relation to plant growth. The presentation showed results in which the group evaluated the effects of metal oxide NPs exposure on the growth of plants and their nutrient content. In addition, results showed the effects of metal oxide NPs exposure on the local soil microbial groups in the plant rhizosphere, which are important for maintaining soil fertility. The studies showed systematic investigation of how the nanoparticle composition, size, and surface chemistry affect their incorporation and toxicity in model crop plant systems. Given their current usage, and the expectation of greater nanoparticle environmental exposure, additional studies that explore the effects of these materials on plant-soil systems in agriculture are needed to evaluate its impact on plant growth, soil fertility, and the sustainability of nanoparticle applications.

Professor Clemens Burda from the Department of Chemistry at Case Western Reserve University gave a talk titled “*How safe are nanoparticles as drug delivery agents? Insights from in-vivo biodistribution and biotoxicity studies,*” that focused on the medical applications of NPs. Inefficient delivery and poor uptake of therapeutic drugs to tumors hamper the efficacy of cancer treatments. Therefore, the “enhanced permeability and retention” (EPR) effect of solid tumors has been explored extensively as a target in the design of drug delivery systems. Cancerous tumors behave differently from normal tissues, having several abnormalities, such as leaky blood vessels and a poor lymph system. It is an important feature that nanosized particles can extravasate from the vasculature and passively accumulate in tumors. Inorganic nanoparticles, especially gold nanoparticles (Au NPs) with tunable sizes and versatile surfaces have received significant attention as drug delivery systems to improve targeting effect and



Professor Clemens Burda

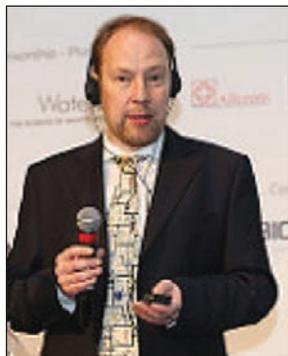
efficacy for cancer treatments. Covalent and noncovalent attachment to the nanoparticle delivery agent are the two major approaches to deliver therapeutic drugs via Au NPs. A covalent attachment approach requires not only structural modification of the therapeutic drugs, but also requires additional trigger signals to control the drug release, such as enzymes, change in pH, or light. Although a significant number of available effective drugs have been modified to covalently bind to Au NPs, the noncovalent attachment maintaining the active drug structure without modification provides an attractive way to bind, deliver, and release the actual drug without needing such triggers. It allows the drug-loaded NPs to passively accumulate in the tumor and the noncovalently attached drug payload to be concentrated in the tumor mass. However, questions arise if the nanoparticle itself could cause complications. Where do the nanoparticles get deposited and how are they affecting the tissue functionality? Can solid, inorganic nanoparticles be excreted? Depending on the respective therapeutics and targets, the drug delivery approach must be chosen carefully.

Finally, a talk given by Professor Petr Fedotov titled “*Nanoparticles of volcanic ash as a carrier for toxic and nutrient elements on global scale,*” focused on the increasing release of nanoparticles (NPs) into the environment. It turns out that about 90 % of atmospheric aerosol NPs are considered to arise from natural sources. In fact, studies have shown that a single volcanic eruption can eject up to 30 million tons of ash. NPs of volcanic ash reach the upper troposphere and the stratosphere and as a result, impact human health, and the environment, including climate. A major area where knowledge is lacking is about the source, behavior, mobility, fate, and toxicity of NPs in the environment. The

main reason is the difficulty to recover NPs from environmental samples for further characterization and quantitative analysis. Actually, the problem of characterization of environmental nano- and submicron particles is directly related to the problem of their separation. In fact, nanoparticles in complex polydisperse environmental samples such as dust, volcanic ash, or soil may represent only about thousandths or less of bulk sample. Therefore, their recovery followed by a quantitative determination of analytes is a complex task. For the first time, a methodology for the separation, investigation, and quantitative elemental analysis of volcanic ash NPs has been proposed. For the separation and recovery of NPs, a combination of the sedimentation field-flow fractionation in a rotating coiled column and membrane filtration was used. The size and morphology of the nanoparticles was characterized using static light scattering and scanning electron microscopy. Contents of macro- and microelements in the initial sample and the obtained fractions were determined by atomic emission and mass spectrometry with inductively coupled plasma. The data showed that the total contents of most elements in the ash sample are comparable to their average content in the Earth's crust. However, in the fraction of NPs (50-100 nm) concentrations of Ni, Zn, Ag, Sn, Sb, Pt, Tl, Pb, Bi are one to two orders of magnitude higher than total contents of these elements in bulk samples. This apparently indicates the pre-concentration of the corresponding elements from the volcanic gases by NPs. In the fraction containing soluble forms of the elements as well as NPs smaller than 50 nm, Cu, Zn, Pb, and several other elements were found; the distribution of elements between the solution and solid phase (NPs) was assessed. The proposed methodology has no analogues and is promising for use in the analysis of volcanic ash and other particulate environmental samples from the various regions of the Globe. It can be also extended to

study on engineered NPs in the environment.

The interaction of nanoparticles with various environmental components must be assessed and systematic analytical methods for doing so, is required. Through this IUPAC symposium the speakers focused on the broad needs for the critical



Professor Petr Fedotov

understanding of the toxicity, bioavailability, and environmental fate and transport of nanoparticles. The symposium speakers will continue this work to provide IUPAC guidelines to support a number of agencies including:

1. Regulatory agencies that are concerned with the risks of nanoparticle disposal and exposure.
2. Chemical industries that use and/or manufacture nanoparticles.
3. Research and government laboratories that are involved in nanoparticle handling and disposal.
4. Toxicology and health groups that aim to understand the transformation of nanoparticles in the environment and the potential risks.
5. Ecological risk assessment groups that need to understand the effects of nanoparticles on the environment.
6. Non-government agencies that are impacted by the growing use and exposure of nanoparticles and the potential risks.

Fate of Pesticides in Latin American Environments (coordinated by John Unsworth)

Agriculture plays a significant role in the economies of Latin American countries, overall Latin American and Caribbean countries account for 24 % of arable land and contribute 11 % of global food production. This region has a diverse and complex range of farming systems due to the wide latitudinal range, varied climatic conditions and different soil types. In general; however, agriculture is characterized by two distinct ways of farming, firstly; commercial farming on large areas of land with the wide scale production of crops such as soybeans, sugarcane, corn, coffee, etc., often as a monoculture and; secondly, smallholding farming, often on family run farms, producing a variety of crops. Pests and diseases pose a significant problem, particularly in the more tropical areas and it has been estimated that farmers lose up to 40 % of their crops because of weeds, insects and fungal diseases. The use of pesticides in this region is, therefore, a necessary tool in reducing crop losses and increasing food production to feed the growing population. However, with the use of pesticides comes the need to ensure that the ecological impact is kept to a minimum. One of the key elements in the safe and sustainable use of a pesticide is to evaluate how likely it is that the environment might be impacted as a result of exposure to the pesticide. It is important, therefore, to understand the growing and climatic conditions, as well as

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the agricultural practices. Thus, for example, it can be expected that if the degradation of a pesticide is temperature dependent, then it will degrade faster under tropical conditions compared to temperate conditions. Similarly, leaching may be more important in areas of high rainfall compared to the drier areas of the region. Properties of the soil (pH, CEC, content of organic matter, etc.) might also differ and affect movement and degradation of pesticides.

Before a pesticide is used, it is important to carry out an environmental risk assessment taking account of local conditions. In Latin America discussions on risk assessment first took place in the 1990s and in 2002 the Andean community published the regulation for registration of pesticides and provided a framework for performing environmental risk assessments. For a risk assessment to be useful it is essential that the data used are relevant and of appropriate quality. These data can come from the registrants of pesticides and from open scientific literature, in this latter case the data may not have undergone quality control or quality assurance and their reliability needs to be assessed before they are incorporated in the risk assessment. The term "risk", when used in the process of risk assessment, has a specific definition *i.e.* "the combination of the probability, or frequency of occurrence, of a defined hazard and the magnitude of the consequences of the occurrence". The assessment is carried out to enable risk management decisions to be made *e.g.*, restricting certain uses of a pesticide. Environmental exposure assessments are carried out using established computer models which determine the likely concentration of a pesticide in the various environmental compartment, soil, water, sediment, etc. Thus, in Brazil, models developed by the United States Environmental Protection Agency have proven to be useful for determining likely environmental concentrations and comparing these to ecotoxicity values to determine the risk to flora and fauna. Validation of models for local conditions is an ongoing process and clearly, as well as good data, a good understanding of their relevance to local conditions is required to give results which equate to pesticide levels to be expected under actual use conditions.

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Speakers at the "Fate of Pesticides in Latin America" Symposium (From left to right: Dr. John B. Unsworth, Dr. Ana Cione, Professor Jussara B. Regitano, Dr. Ximena Patino, Dr. Rafaela M. Rebelo, Professor Keith R. Solomon)

Advanced Materials (POLYCHAR2017)

by Chris Fellows and Melissa Chan Chin Han

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The 25th **World Forum on Advanced Materials** (POLY-CHAR2017) (derived from **POLY**mer **CHAR**acterization), under the auspices of the Scientific Committee of World Forum on Advance Materials and International Union of Pure and Applied Chemistry (IUPAC), was hosted by the Institut Kimia Malaysia at the Putra World Trade Centre, Kuala Lumpur, Malaysia on 9-13 October 2017. A total of 2 plenary, 99 invited, 55 oral, 48 posters and 21 participants from 31 countries were recorded. With the significance of the 25th anniversary of the series, it was an occasion for more than usual