February 2016
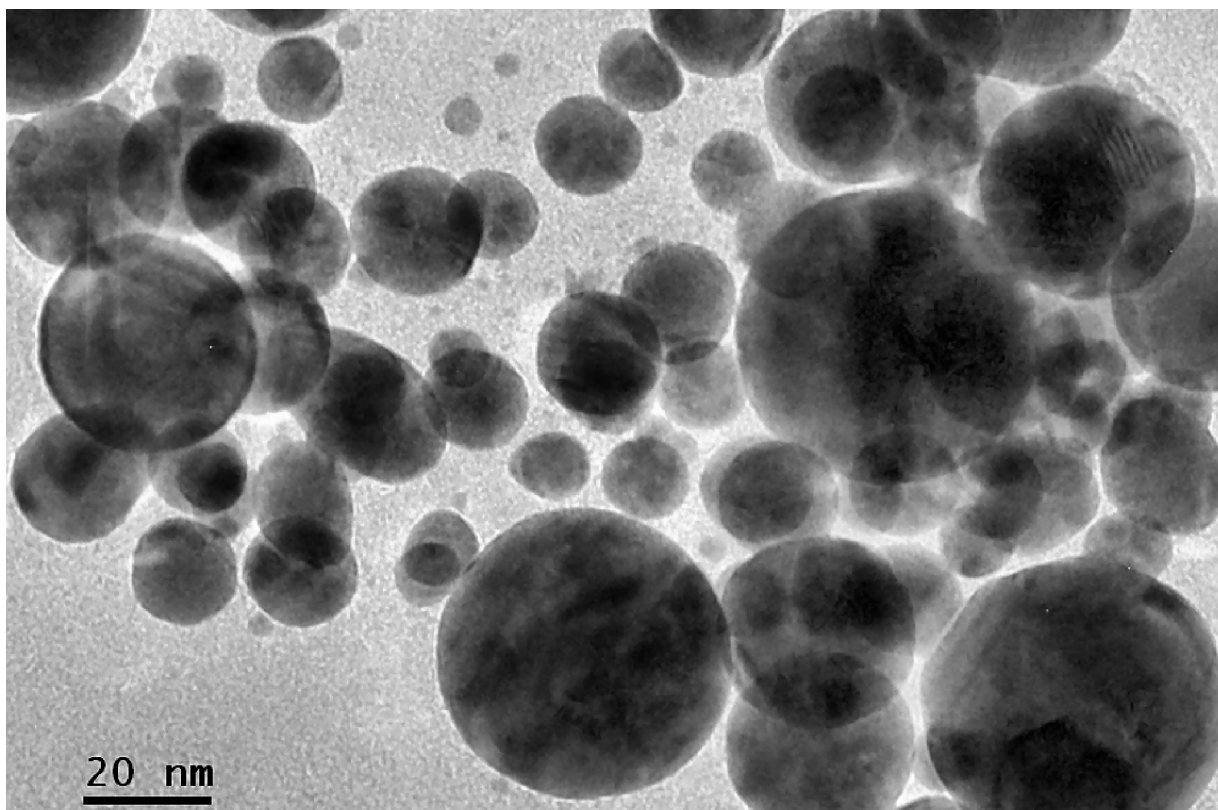# ECG *Bulletin*

Nanomaterials in the environment. Following our successful Distinguished Guest Lecture and Symposium in 2015, we publish a meeting report and three articles on the implications of increasing nanoparticles use on the environment (pp. 11-20). Eugenia Valsami-Jones, the 2015 Distinguished Guest Lecturer, warns that laboratory studies only partially capture the complexity of real environments (pp. 13-15).
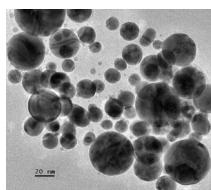
Environmental Briefs. We continue our series of short updates on important environmental techniques with articles on remote sensing of thermal IR radiation to determine atmospheric composition (Harjinder Sembhi, pp. 21-22), and on biotic ligand models for predicting trace metal concentrations in the water column (Adam Peters and Graham Merrington, pp. 23-24).

Also in this issue. Two book reviews discuss, respectively, the historical processes that brought our planet into the Anthropocene (p. 6) and the pros and cons of fracking (p. 7).

Contents

Cover image: Gold nanoparticles imaged with a transmission electron microscope. Credit: Georgy Shafeev/Shutterstock

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This and previous issues of the ECG *Bulletin* are available without charge at www.rsc.org/ecg. For ECG membership details, visit www.rsc.org/MembershipECG

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Chairman's report

News from the ECG

In 2015, the Environmental Chemistry Group organised several well-attended meetings, including the Distinguished Guest Lecture and Symposium on nanomaterials in the environment. We also celebrated the 20th anniversary of the ECG *Bulletin* and continued to expand our ECG Environmental Briefs series.

2015 ECG Distinguished Guest Lecture

Our Distinguished Guest Lecture and Symposium, held on 24 June 2015, was entitled "Nanomaterials — environmental remediants or toxicants?" Organised by Rowena Fletcher-Wood and the ECG committee, this well-attended meeting included talks by Dave Spurgeon, Debra Rodrigues and Iseult Lynch. In her Distinguished Guest Lecture, Éva Valsami-Jones (University of Birmingham) highlighted the complexities of assessing the environmental impacts of nanoparticles and outlined how progress can be made. A report of the meeting and articles from the speakers are included in this issue.

The 2016 ECG Distinguished Guest Lecture will be held on 22 March 2016. The theme this year is 'Geoengineering the Climate', and the Distinguished Guest Lecturer is Alan Robock (Rutgers University). Our three supporting speakers are equally excellent (Joanna Haigh, Imperial College, David Santillo, Greenpeace and Michael Stephenson, British Geological Survey). More information may be found at tinyurl.com/om755cq and on p. 10 of this edition. Book soon as places are limited.

Other meetings

Two excellent meetings were co-organised by your committee members this year: the *New Developments in the Analysis of Complex Environmental Matrices 2015* meeting was held on 6 February 2015 at Burlington House in London. And on 4 March 2015, consultants, regulators and scientists met in Sheffield for a one-day meeting on *Emerging contaminants in waters and soils, practical considerations – sampling, analysis and consequences*. Meeting reports may be found in the July 2015 ECG *Bulletin* (tinyurl.com/ecgb2015-07). Suggestions from members of possible meeting topics are welcome and should be directed to the ECG Secretary, Zoë Fleming (zf5@leicester.ac.uk).

ECG *Bulletin*

The ECG *Bulletin* is an exciting mix of articles on environmental concerns, meeting reports, environmental briefs, and ECG news. The January 2015 anniversary edition included special articles on the past 20 years of environmental chemistry and of the *Bulletin* (see tinyurl.com/http-ecgbarchive).

ECG Environmental Briefs

With the latest articles on pages 21 and 23 of this edition, our Environmental Briefs series now contains eleven articles. We have had much positive feedback about these brief, informative, expert-written articles that explain widely used techniques and approaches in environmental chemistry in an accessible way. All articles may be viewed and downloaded from tinyurl.com/pun38tf. I was pleased to find that if you Google "Environmental Briefs", our series comes out as the top hit. I also understand they have been used in the teaching of at least two university environmental science courses. All members are encouraged to let us know what topics you would like us to cover.

Funding the ECG

All of the above happens through the work of your committee members, who meet four or five times a year in Burlington House. A recent review of Interest Group funding means that our funding will be significantly reduced. Unfortunately, under the new formula we would not have sufficient budget to cover our annual travel. As we are the largest RSC interest group and one of the most active, we are engaging with staff at the Royal Society of Chemistry on how we might secure more funding to support all our meetings and activities.

ECG committee changes

As reported in a previous ECG *Bulletin*, the committee has recently changed. I would like to particularly thank the outgoing chair, James Lymer, for his hard work over the past decade as member and recently chair of the ECG committee. James has organised numerous meetings and provided close links with the toxicology special interest group; he was also a regular contributor to the ECG *Bulletin*. I would also like to thank Jo Barnes and Cecilia Fenech, respectively, for their contributions as ECG Treasurers.

Martin King, ECG Chair

Article

From environment to outreach

Rowena Fletcher-Wood (Science Oxford, rowena.fletcherwood@gmail.com)

Researchers are best placed to explain scientific issues to interested members of the public. In recent years, I have been involved in several activities that brought environmental science to a wider audience.

In May 2014, I was part of a team organising Cambridge's **Pint of Science** on *Earth and Environment*, sponsored by the RSC and University of Cambridge. Our speakers included Professor Eric Wolff (a former ECG Distinguished Guest Lecturer) from the British Antarctic Survey, whose research into isotopic abundances and impurity phases in ice cores allows him to dig deep into earth and climate history. The lectures were part of a three-day science gatecrash of pubs in cities around the world that was started in 2012 and runs annually (see pintofscience.co.uk/about). Participating pubs convert back rooms into informal lecture theatres for just three nights, where researchers come to give public talks on what they do. In 2015, Pint of Science expanded, and for the first time took place in Birmingham, where I was then living. Pubs across the city centre—including the cosy upstairs gin bar of the quirky Jekyll and Hyde, where Café Scientifique is held—came alive with inspirational ideas, discussion and narratives of scientific venture. The distribution, intensity and ongoing demand for Pint of Science show how willing the public are to engage in science, especially with a beer in hand. The next Pint of Science Festival will take place from 23 to 25 May 2016. Look out for events near you.

Early career researchers can also share their research through a range of channels. One such channel is the **Brilliant Club** (www.thebrilliantclub.org), an award-winning organisation that pairs PhD students and postdoctoral researchers with small groups of school children aged 10 to 18 from state schools from which few students enter highly selective universities. The goal is to increase the numbers of children going to highly selective universities from these schools. The researchers teach a short, intense course on their own research topic and set a final assignment highly challenging for the children's age group. In 2015, I taught "Environmental Science: Controversy and Chaos" to 24 Birmingham pupils in years 9 and 10, blasting through environmental issues that included the nuclear industry, biofuels, CO_2 storage, human impacts on climate, measuring the past climate, and plastic waste. We also talked about social issues surrounding the environment, such as human and economic bias, uncertainty and extrapolation, the value of consolidating evidence, the role of the media, science in advertising, and what "natural" really means. Debate-focussed, the course transitioned from teacher-led to student-led; by the end, I simply gave them some text or a video and watched what they did with it. In their final assignment, the pupils achieved a range of grades from 3rd class to some impressive 1st classes. Early career researchers interested in taking part in this program can get in touch via email (hello@thebrilliantclub.org).

More recently, I have been experimenting with my brand new **Science Jigsaws**. Pictures kindly provided by friends and researchers are laid onto wooden bases and cut by family-run Puzzleplex (puzzleplex.co.uk/), who create unusual shapes rather than the usual squares to make jigsaw building more challenging and thoughtful. Amongst my small custom collection are such pieces as

"The Sun" and "Climate Change". A picture taken by my uncle and keen nature photographer, Kevin Meehan, "Climate Change" shows a range of spiky icebergs along the coast of Iceland. I've tried the jigsaws on adults and children, for example
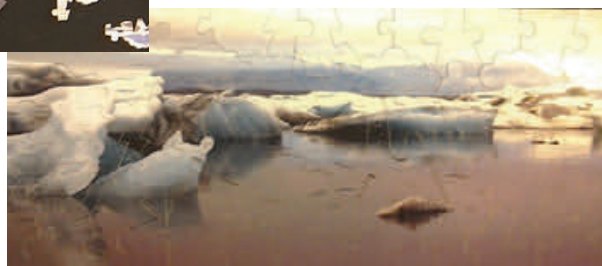
at postgraduate training days and after-school clubs, inviting questions such as "How fast is the ice melting?" or asking them what they know already. As land ice melts, land height rises at 1.4 inches per year according to global positioning system measurements. But what does this mean to young people, and how do they understand the changing climate through stories, images, and science? Motor learning—doing a jigsaw whilst gathering information—is a good way to integrate ideas and creates long-term sensory memories; jigsaw learning can be adapted to any audience.

The ECG Interview: Tom Sizmur

ECG committee member Tom Sizmur is a Lecturer in Environmental Chemistry at the University of Reading. He tells us about his career as a soil chemist.

What inspired you to become a scientist?

I have always been interested in how nature works. The natural world is fabulously complicated and there are so many interacting factors that govern the functioning of environmental systems. As a scientist, I strive to understand these factors so that we can predict future changes to our environment.

How did you come to specialise in soil chemistry?

During my undergraduate degree, I became interested in how soils worked and how they are affected by environmental pollutants. I still find it amazing that, as a scientific community, we seem to know more about the stars in the sky than we do about the biogeochemical interactions that occur in the soil beneath our feet. I recognised early on that there was an urgent need to better understand how soils deliver nutrients to plants and how they are able to filter or degrade pollutants. I have dedicated my professional life to understanding how organisms interact with the chemical and physical constituents in the soil. This knowledge will help to understand how they are able to support life aboveground.

Could you describe your current job?

I spend roughly half of my time teaching BSc and MSc students the fundamental concepts that underpin environmental chemistry and environmental pollution. I also teach in the field so students can explore environmental issues beyond the laboratory and practise collecting and analysing samples. The idea is to help them develop the skills they will need to become environmental consultants, regulators and research scientists when they graduate. The other half of my time is spent on research into how organisms interact with their chemical and physical environment. In much of this research I have focused on how earthworms engineer the soil environment in which they live. Earthworms create burrows and deposit casts on the soil surface. These processes change the biogeochemistry of the soil. During my PhD, I showed that the mobility of metals in soil increases after passage through the earthworm gut.

What advice would you give to anyone considering a career in environmental chemistry?

Don't focus on trying to solve a particular environmental issue or answer a specific question that is close to your heart. The likelihood is that as your career develops, new and interesting challenges will emerge. For example, when I was a BSc student climate change was top of the agenda. Now, issues surrounding sustainable intensification of food supply are receiving a lot of attention. The skills required to address both issues are similar, because they are both complex interdisciplinary environmental issues. The key to success is to develop a set of capabilities that can be applied to whatever the next big challenge is.

What are some of the challenges facing the environmental chemistry community?

Translating research into practical solutions to environmental issues is a big challenge. For many years, environmental scientists have established a reputation for identifying problems rather than developing solutions. This has resulted in disengagement with industry. We now need to work together to develop solutions to environmental issues.

What is the most rewarding aspect of your career so far?

I still get a buzz when seeing scientific data for the first time. I often cannot wait to plot it on a graph to see if it supports the hypotheses we are testing. There is nothing more rewarding than making a discovery and, for a moment, being the only person in the world who knows it.

If you weren't a scientist what would you do?

Since becoming a lecturer, I have discovered a passion for teaching. It is very fulfilling to mentor students in their learning. If I had not become a scientist, then I hope I would have considered a career in teaching.

Book Review

The Shock of the Anthropocene

Julia Fahrenkamp-Uppenbrink (ecgbulletin@hotmail.co.uk)

Have we entered a new epoch in which humans dominate geological processes at the Earth surface? The pervasive impacts of humans on all aspects of the environment show no sign of abating, with potentially devastating consequences for humans and wildlife. The term for this epoch—the Anthropocene—appears to suggest that it is an inevitable outcome of our growing population and advanced state of civilization. In *The Shock of the Anthropocene*, historians Christophe Bonneuil and Jean-Baptiste Fressoz show that far from inevitable, today's situation results from political and economic choices made despite concerns about the environmental impacts raised since the early days of the industrial revolution.

A defining feature of the Anthropocene is the rise in carbon dioxide and the resulting climate change; other factors include the rapid loss of biodiversity and changes in biogeochemical cycles as a result of artificial fertilisation. However, *The Shock of the Anthropocene* does not provide simple answers or a single narrative for how to respond to these interrelated crises. This is entirely intentional, as the authors aim to portray the many different ways in which our current epoch can be understood and illuminated. In the process, they use alternative terms for the Anthropocene that initially seem cumbersome but arguably better capture the driving forces behind the environmental destructiveness of modern life.

One such term, the Thermocene, is used to chart the history of energy use. In the early 19th century, large hydraulic projects provided energy for the growing textile industry in northern England and Scotland at lower prices than for coal. In the US, state-of-the-art wind mills played a key role in the agricultural development of the Midwest in the 19th century, while the 1920s and 1930s saw the development of solar water heaters and low-energy homes that provided large potential cost savings. Yet, fossil fuels won out in these and many other cases, with solar, water and wind energy reduced to "alternative energies" that are only now seeing a renaissance. Bonneuil and Fressoz argue

that the reasons were often ideological and political rather than technological. In the case of the British textile industry, coal provided a decentralised source of energy that did not require coordination between the entrepreneurs of the early industrial revolution. Wind and solar power in the US lost out in the 1950s, when powerful electricity companies had a strong interest in extending the national grid to all consumers.

Antique aermotor windmill. Credit: Kenneth Kiefer/Shutterstock

Other chapters explore the role of war and the military (the Thanatocene), consumerism (the Phagocene), and the prevalent economic system (the Capitalocene) in bringing about the Anthropocene. But perhaps most interesting from the point of view of environmental chemistry is the history of environmental warnings that went unheeded. Today's environmental scientists are far from alone in their concern for the environment. As early as 1778, George-Louis Buffon wrote that "the entire face of the Earth today bears the imprint of human power" and warned nations not to "use everything up without renewing anything." And in 1913, Edmond Perrier asked whether "we have the right to monopolise the Earth for ourselves alone, and to destroy for our profit... everything it has produced that is finest and most powerful." These words retain their relevance today.

Rather than considering ourselves the masters of our environment, humans will need to, in Bonneuil and Fressoz's words, place nature "at the heart of our conception of freedom." Given today's dominant consumerism, this may seem unlikely. But by laying out the many factors and circumstances that brought about our current predicament despite knowledge of the detrimental effects, *The Shock of the Anthropocene* helps the reader to conceive of a different future in which nature is no longer seen as separate from humanity.

Book Review

Fracking: Issues in Environmental Science and Technology No. 39

Cecilia Fenech (Cranfield University, c.fenech@cranfield.ac.uk)

Shale gas hydraulic fracturing (fracking) is considered by some to be essential for securing our energy future and increasing the energy mix, while others consider it highly damaging to the environment. Fracking is thus both controversial and topical, particularly in the UK, where it is not yet practised on a commercial basis, but is receiving high-level support. This book, edited by R. E. Hester and R. M. Harrison, aims to outline both sides of the debate with contributions from scientists, policymakers, and industry.

Each of the eight chapters is a stand-alone piece written by a different author or group of authors, allowing the reader to get a deeper understanding of a specific angle of the debate. The book as a whole provides a comprehensive understanding by combining more technical sections (e.g. including details of fracking operations and hydraulic wells) and less technical policy sections related to shale gas operations around the world. Each chapter is also well-referenced,

Credit: Serz_72/Shutterstock

enabling readers to explore the concepts further. This makes the book accessible to readers with differing purposes, from a passing interest in the fracking debate to a requirement for a deeper understanding of more technical aspects.

The book starts with an overview of the role that shale gas may play in securing our energy future. As Peter Hardy (UK Institute of Gas Engineers) explains, fracking is widely touted as the answer to depleted natural gas deposits as it enables the economical extraction of unconventional shale gas. However, fracking brings with it a number of environmental, human health, and safety concerns.

Concerns relate to the chemicals used in the fracking process and their disposal, greenhouse gas emissions; and the hydraulic fracturing process itself, which has been linked to earthquakes in the vicinity of such activities.

The following chapters explore the economic impacts of shale gas in the USA (F. Taheripour *et al*, Purdue University); considerations for shale gas and shale oil exploration (I. Scotchman, Statoil); climate change impacts (J. Broderick & R. Wood, Tyndall Centre for Climate Change Research); hydrogeological aspects of UK extraction (R. Ward et al., British Geological Survey); the Australian experience with coal seam gas recovery (A. Randall, University of Sydney); and Chinese prospects for shale gas (S. Jiang, University of Utah). In the final chapter, T. Bosworth (Friends of the Earth) argues that shale gas is "unburnable and unwanted" as its environmental concerns far outweigh any potential benefit. Although the book has a UK focus, chapters relating to the experiences in different countries (USA, Australia and China) broaden its scope considerably. These chapters also highlight the specific considerations that may make shale gas hydraulic fracturing suitable or unsuitable depending on the circumstances.

The use of shale gas in the UK is still in its infancy, and a number of hurdles remain to be overcome prior to commercial success. How far should the UK go to overcome these hurdles while taking into account health and other concerns? What role should shale gas play in the UK's energy mix—a key energy source for the foreseeable future, a transitional fuel, or none at all? The book does not give answers to any of these questions, but rather provides an illuminating overview of both sides of the debate, allowing the reader to form an educated opinion.

Meeting report

Contaminated land and extreme weather conditions

Rowena Fletcher-Wood (Science Oxford, rowena.fletcherwood@gmail.com)

A one-day meeting on "Contaminated Land and Extreme Weather Conditions" was held in the CIRIA (Construction Industry Research and Information Association) offices in London on 29 June 2015. Attended by *ca.* 35 scientists and policymakers, the meeting highlighted key concerns about contaminated land that had been overlooked in the past and showed that fundamental changes must be made to industry structure and the paradigm of safety assessment.

The meeting began with a talk by the CIRIA chairman, Mike Ellis, who spoke about the urban soils of central London. He examined the difficulty found separating "soil" from "dust" and considered how the spatial distribution of contaminants varied with the nature of contaminants. For example, lead and arsenic correlate not only with urban density, but also with the natural background, determined by rock types in the area. He further mentioned a 1:1 observed correlation between bioavailability and bioaccessibility of contaminants, and queried the validity of separating these concepts. Other points included the difficulty found in assessing hazard on a reasonable time scale. For example, a New Orleans study has shown a 22-year lag between atmospheric lead pollution and its consequences upon human health and behaviour—in this example, an increased aggravated assault rate.

Subsequent speakers discussed contaminated land in the context of sustainable development and highlighted the reasons why predicting environmental changes and minimising the detrimental effects of development are not straightforward. For example, they touched on the uncertainty in model predictions of future CO_2 emissions

> A New Orleans study has shown a 22-year lag between atmospheric lead pollution and its consequences upon human health and behaviour.

and the different drivers for fossil fuel reduction at regional and national scales, such as local flood risk and the cost of technological changeover. Correct identification of catchments for remediation treatment requires knowledge of factors such as wind speed and direction, historical land use (e.g. mining legacy), and pH-dependent soil leaching. This highlights the intricacy of integrated risk analysis. Good sources of information include the research-policy partnership LWEC (Living with Environmental Change) ([1]) and the European IPPC bureau (Integrated Pollution Prevention and Control) ([2]).

Briony Turner (ARCC, UKCIP) and Joanne Kwan (CIRIA) highlighted the absence of contaminated land and remediation strategies in the government's Climate Change Risk Assessment (CCRA) report ([3]). They called for a statutory reporting process to develop a body of data, as well as shared learning and guidance documents. With funding from the EPSRC, the UKCIP ARCC network aims to fill these gaps. For example, increasing river erosion under climate change may release more contaminants. Yet, contaminant mobility is not currently monitored in the field and is in fact very difficult to monitor, because contaminants cross river catchments and require very sensitive detection as they are diluted and dispersed. The speakers also reported on STEM workshops in schools that educate pupils about the impacts of climate change.

Oliver Lancaster (Wales & West Utilities Ltd) focussed on extreme weather, the implications of intense flooding and protection, and policy and practices involving groundwater. Lancaster expressed concern over how we assess contaminated land and classify contaminants and develop conceptual site models. Safety assessments generally include the caveat "based on current site use and land conditions," but these sites may be subject to variation under continuing climate change and varying weather patterns. Future increases in rainfall may even invalidate safety assessments, although, Lancaster added, "Given the uncertainty, it would be a very bold consultant

Winter flood. *Flood waters threaten the surrounding roads and housing as the Afon Teifi river bursts its banks in December 2013. Floods like this can mobilise contaminants. Credit: i4lcocl2/Shutterstock*

the flow, temperature and volume of surface water, but also its "rebound time" for recovery after contamination. Previous estimations of hydrological behaviour have been proven erroneous. In one example, the estimated time for contaminated water to recover was 1 year, but the actual recovery time was only 6-8 weeks. It is questionable whether we can validate any predictions without greater knowledge of why this occurred. Small errors in one set of predictions can make huge differences in the premises of another, leading to disjointed models between industries and academic experts.

to suggest climate change-driven remediation measures". Taking the aspect of flooding further, Chris Meakin (WorleyParsons) argued that flooding causes and exacerbates contamination. Predictions of future climate change include the possibility of an increase in extreme weather events. He cited the winter of December 2013 to February 2014 as a warning example; the wettest winter on record, it saw storms and floods throughout the country. To address and mitigate the risk of flooding contaminated land, Meakin called for a change in perception of conceptual models, such that risk assessments become flexible, living documents, rather than pre-set standards, and greater uncertainty is managed with incremental improvements as more data become available. For this to be successful, integrating knowledge and expertise across industries is vital. Potential problems with this approach include the need to risk-assess changing methods, essentially producing risk assessments of risk assessments, and the sparsity of current research and guidance. CL:AIRE (Contaminated Land: Applications in Real Environments), the Forestry Commission and CIRIA are existing bodies that are pursuing this work.

Stephen Kidley (Celtic Ltd.) explained that knowledge of groundwater in the UK is patchy, with research lagging years behind that on surface water. The study of groundwater is more complicated than that of surface water and cannot be simplified to two dimensions. Rock permeability plays a key role in the three-dimensional movement of water. Not only does groundwater affect

Trevor Howard (EA) provided the regulator's point of view, highlighting additional outcomes of climate change on contaminated land that are worthy of consideration. Under elevated temperatures and increased rainfall, organic matter breaks down faster and may produce different degradation products; the concentration of metal toxins in plants may also vary, as may the fixation of metals in soil, which depends on soil pH and relative humidity. On the streets, tar is more likely to melt, and toxic metals such as mercury may vaporise from contaminated sources. Biotic and chemical processes will also change, but the extent to which this will occur has not yet been estimated with any confidence. Because climate change increases variability, the most variable climates – like that in the UK – remain the hardest to model.

This meeting is part of a series of events organised by CIRIA.

For future CIRIA events visit: www.ciria.org/

References

1. www.rcuk.ac.uk/research/xrcprogrammes/lwec

2. http://eippcb.jrc.ec.europa.eu/reference/

3. www.gov.uk/government/publications/uk-climate-change-risk-assessment-government-report

2016 Distinguished Guest Lecture & Symposium:

Geoengineering the Climate

A one-day symposium organised by the Environmental Chemistry Group of the Royal Society of Chemistry

Where: The Royal Society of Chemistry, Burlington House, Piccadilly, London
When: Tuesday 22nd March 2016, 12.00 pm - 17.15 pm. Lunch is provided.

Confirmed speakers

Professor Joanna Haigh (Imperial College London)
"Climate geoengineering: some fundamentals"

Dr David Santillo (Greenpeace Research Laboratories)
"Climate geoengineering: how could it be regulated?"

Professor Michael Stephenson (British Geological Survey)
"Climate geoengineering: carbon capture and storage"

Distinguished Guest Lecture: Professor Alan Robock (Rutgers University)
"Smoke and mirrors: not the solution to global warming."

Professor Robock will deliver the 2016 ECG Distinguished Guest Lecture, speaking on solar radiation management (SRM) by injecting particles into the stratosphere, brightening clouds, or blocking sunlight with satellites between the sun and Earth. If there were a way to continuously inject SO_2 into the lower stratosphere, it would produce global cooling, stopping melting of the ice caps, and increasing the uptake of CO_2 by plants. Although no systems to conduct stratospheric geoengineering now exist, a comparison of different proposed injection schemes, using aeroplanes, balloons, and artillery, shows that putting sulfur gases into the stratosphere would be inexpensive. But there are at least 27 reasons why stratospheric geoengineering may be a bad idea. These include disruption of the Asian and African summer monsoons, reducing precipitation to the food supply for billions of people; ozone depletion; no more blue skies; reduction of solar power; and rapid global warming if it stops. Furthermore, there are concerns about commercial or military control, and serious degradation of terrestrial astronomy and satellite remote sensing. Global efforts to reduce anthropogenic emissions (mitigation) and to adapt to climate change are a much better way to channel our resources.

Delegate Rates

Non-members of ECG: £35 (£25 early bird rate before 12 Feb)
ECG members and concessions: £30 (£20 early bird rate before 12 Feb)

A limited number of free places are available for members, e.g. the unemployed. If you would like to apply for one of these places, please contact the meeting organiser.

To register online, please visit events.rsc.org/rsc/833/register before 14th March. Delegate fees are non-refundable. For enquiries, contact the meeting organiser, Rowena Fletcher-Wood (ecg.dgl@gmail.com).

Meeting report

2015 Distinguished Guest Lecture and Symposium: Nanomaterials— environmental remediants or toxicants?

Steve A. Leharne (University of Greenwich, s.a.leharne@gre.ac.uk)

Recent reports released by Research Councils UK and the Royal Society of Chemistry have stressed the importance of nanoscience and technology to the long-term prosperity of the UK. On 24 June 2015, a half-day symposium convened by the ECG considered the environmental challenges and benefits provided by the synthesis and use of nanomaterials. The symposium, attended by about 60 people, also provided the occasion to present the ECG's DGL medal to Professor Valsami-Jones from the University of Birmingham.

David Spurgeon (Centre for Ecology and Hydrology, Wallingford, UK) examined the benefits and problems associated with the use of standard tests for assessing nanomaterial ecotoxicity. Standard tests are used to ensure inter-laboratory data comparability, and are approved *inter alia* by the OECD. Many commercially used nanomaterials end up in sewage sludge (see the photo below), which is spread onto soils. Thus, nanomaterial contamination is very often a soil contamination issue. Standard tests exist for examining the ecotoxicity of nanomaterials in soils. These tests rely upon the use of a limited number of test species (normally adults); a standard medium; and standard test conditions to examine a particular

toxicological end-point (normally death) over a defined, short-term exposure period. The speaker showed that such standardised tests very often fail to identify critical factors that may affect toxicity in different environments and over different time scales. For example, soil pH and organic matter composition attenuate nanoparticle toxicity in soils. One study found that silver nanoparticles become increasingly toxic to the earthworm *Eisenia fetida* as they changed with time (aging). Because standard tests rapidly generate data and provide reliable information for initial risk assessments, they are the tools of choice for regulatory risk assessment. However, such tests restrict the diversity of data available for risk modelling and can fail to address key endpoints and effects. Non-standard tests can be important for detecting specific outcomes and validating hypotheses.

Iseult Lynch (University of Birmingham) was a last minute replacement for Dr Tom Scott, who was unable to attend. She focussed on nanoparticle interfaces, which are key to the environmental fate and behaviour of

Waste water treatment plant. Nanoparticles often end up in sewage sludge that is spread onto soils. Credit: SKY2015/Shutterstock

nanoparticles. Nanoparticle interfaces have high surface energies. Molecular adsorption lowers surface energy and thereby passivates the interface. Humans can take up nanoparticles by ingestion, inhalation or absorption through the skin. After entering the body, nanoparticles are surrounded by biological fluids. Binding of biomolecules to the nanoparticle surface can confer biological recognition. The resultant biomolecule/nanoparticle complexes can act as "Trojan Horses" for the transport of contaminants. In the environment, nanoparticles are also able to bind organic matter. Binding of biological or organic molecules may stabilise nanoparticles against aggregation or may promote it. The range of effects associated with molecular binding must be assessed to properly understand the environmental fate and toxicological properties of nanoparticles.
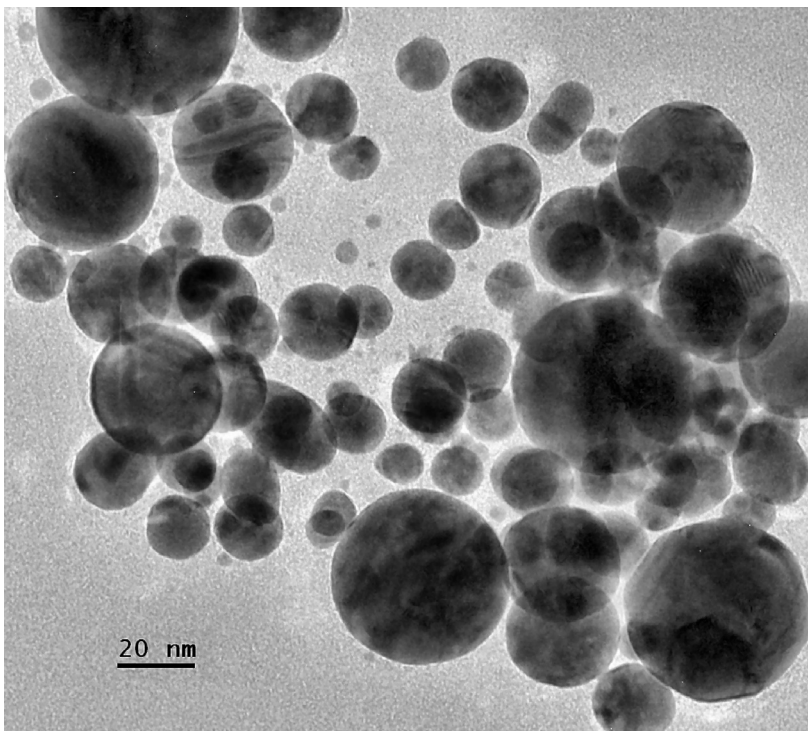
Gold nanoparticles imaged with a transmission electron microscope. Credit: *Georgy Shafeev/Shutterstock*

Debora Rodrigues (University of Houston) spoke about her group's work on using carbon-based single-walled and multi-walled nanotubes and graphene and graphene oxide for the sustainable remediation of wastewater (see photo on the previous page). The main goal is to produce cheap nanomaterials that are readily dispersed in water and that have reduced human cytotoxicity. In toxicity measurements against human cell lines, graphene oxide functionalised with poly(N-vinyl carbazole) (PVK) showed no toxicity, and carbon nanotubes functionalised with PVK showed reduced toxicity compared to the nanomaterials without PVK. Functionalisation of the carbon nanomaterials with PVK permits the removal of metal ions such as lead under appropriate pH conditions (pH 5). The same materials were able to inhibit microbial activity. The speaker also showed that the functionalised nanomaterials can be attached to membrane filters. Filters containing PVK-functionalised carbon nanotubes were effective in inactivating/killing bacterial cells through cell disruption, resulting in better quality water (though possibly not of drinking water quality). Unfortunately it remains difficult to regenerate the nanomaterials. These materials show promise but issues of cost and large-scale production need to be addressed.

The meeting closed with the 2015 Distinguished Guest Lecture by **Eugenia (Éva) Valsami-Jones (University of Birmingham)**. She began by outlining the perceived economic potential of nanomaterials, which arises from their novel properties, including quantum confinement, surface plasmon resonance and superparamagnetism. However, their toxicity is difficult to predict because of major challenges of detection and characterisation. For example, nanoparticle size, shape and structure is affected by aging. Moreover, characterisation needs to be undertaken in relevant media. A particular challenge lies in assessing the uptake of metals from metal-based nanomaterials (see micrograph) at realistic exposure levels.

To address these challenges, Éva Valsami-Jones outlined the use of nanomaterials that have been either isotopically or fluorescently labelled. In one study, labelling permitted an assessment of zinc assimilation via dietary exposure. One conclusion from this work was the absence of any "off-the-scale" toxicity associated with nanoparticles. Nanoparticles may be internalised through a range of biological mechanisms, including phagocytosis for large particles, endocytosis for smaller particles, and macropinocytosis from fluids. Surface-coated nanoparticles can also be taken up by biological cells. Computer modelling shows that surface energy falls with increasing numbers of atoms, but this reduction is not smooth. Thus, apparent inconsistencies in reactivity data with size may arise from genuine changes in surface properties with particle size.

DGL Article

Nanomaterials: Small particles, big trouble?

Eugenia Valsami-Jones (University of Birmingham, e.valsamijones@bham.ac.uk)

Nanotechnology is proliferating in all aspects of modern life. Novel nanometre-scale materials are used in every-day products from cosmetics and medicines to fitness and food products. Research into the safety of these materials is lagging behind their technological applications, leading to concerns that products become available without due environmental and human health safety considerations. Furthermore, research into nanomaterial safety is marred by controversy. Consensus is lacking on laboratory methodologies, long-term studies are few, and approaches to develop nanomaterial groupings and models of activity are in their infancy. Thus, nanomaterials, despite their small size, are the source of big trouble.

It has been more than 10 years since the term "nanosafety", describing research into the potential health and environmental threats from nanomaterials and the development of safer alternatives ("safe by design"), became a regular feature of the scientific literature. Key to the recognition of the need for such research was an authoritative report published by the Royal Society and the Royal Academy of Engineering in 2004 (*1*), which presented in technical detail concerns about the risks of nanotechnology, particularly free engineered nanomaterials. Other major reviews followed, including EPA's Nanotechnology White Paper in 2007 (*2*) and a report by the Royal Commission on Environmental Pollution in 2008 (*3*) that described the issues and lack of progress since the RS&RAE report (*1*). In 2012, the Royal Society of Chemistry published its own review of nanosafety, particularly focussing on the difficulties in developing legislation in the lack of sufficient and sound scientific evidence (**Figure 1**) (*4*).

Concerns about the need for research, not only to understand potential hazards from nanomaterials, but also to develop an appropriate framework to regulate them, are well justified. An estimated 500 to 2,000 nanomaterials were placed on the EU market at volumes of at least 1 tonne/year in the period from 2012 to 2014 (*5*). This trend is likely to continue or even increase, and these nanomaterials are consequently affected by registration obligations under the chemicals' safety framework known as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), which entered into force in 2007. About 10% of these nanomaterials are untreated nanoforms of a bulk material that is already registered (*5*). Testing these nanomaterials and updating the registration
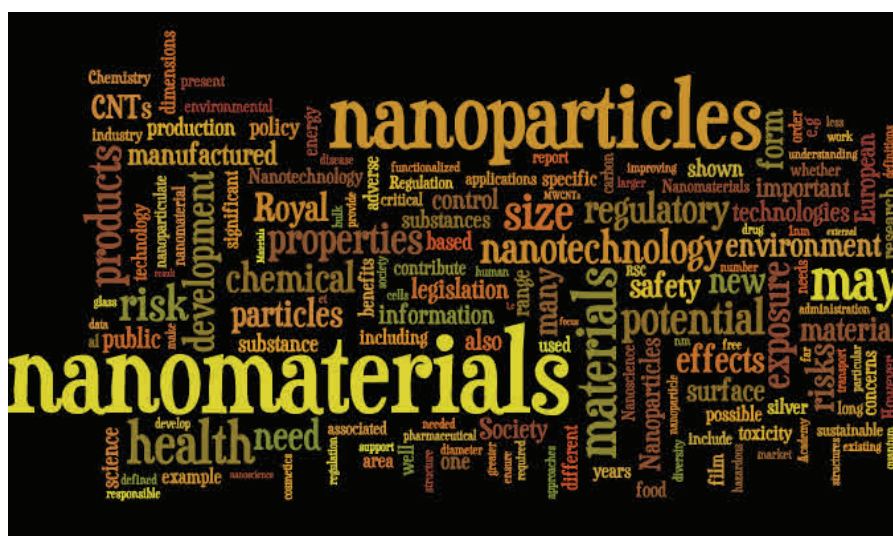
Figure 1. Wordle using the text from Nanotechnology Position Document, 2012

dossiers would entail costs of between €50 million and €315 million based on the proposed amendments to REACH guidelines for nanoforms. Additional costs between €6 million and €38 million per nanomaterial are expected for the 450 to 1,800 surface-treated nanoforms (variants around a common core material), leading to total costs of up to €600 million to be borne by industry, mostly (around 80%) small and medium-sized enterprises (*5*). Development of a framework that would enable grouping and read-across approaches validated for nanomaterials is therefore a major research priority.

In my 2015 ECG Distinguished Guest Lecture, I focus on two aspects of my research that are contributing to alleviating uncertainty on the safety of nanomaterials.

Stable isotope labelling

Isotopic labelling of nanomaterials allows them to be traced in toxicity experiments. There are two main ways of labelling nanomaterials:

Labelling relying on optical tracing. This involves fluorescent labels that are either grafted on the nanomaterial's surface or (in the case of the very small quantum dots) result from the nanomaterial's intrinsic fluorescence.

Labelling relying on chemical tracing. Here, the label is a rare element or isotope that is usually introduced during nanoparticle synthesis and that is therefore homogeneously distributed in the nanomaterial.

The development of a number of stable isotope-labelled nanomaterials enabled us to understand better the ecotoxicity of nanomaterials in experiments designed to simulate realistic exposure of organisms to nanomaterials. For example, the development (*6*) and testing (*7*) of ZnO nanoparticles labelled with the stable isotope ^{67}Zn allowed us to show that zinc from isotopically modified ZnO nanoparticles is efficiently assimilated by freshwater snails (**Figure 2**) when ingested with food. Agglomeration of the nanoparticles did not reduce bioavailability and did not preclude toxicity. The ZnO nanoparticles damaged digestion.

In more recent studies using isotopically labelled CuO (*8*) and Ag (*9*), we have demonstrated the increased sensitivity that isotopic labeling provides. This is important because experiments can now be performed at environmentally relevant concentrations. As a result, exposures are more realistic and the true toxicity mechanisms can be identified and distinguished from the result of excessive dosing. In the case of Ag nanoparticles, isotope mass balance calculations show

Figure 2. Limnaea stagnalis, the freshwater snail used in the studies discussed here (7, 8). Credit: Marie-Noële Croteau, US Geological Survey

that labelling increases tracing sensitivities at least 40 times and possibly up to 4000 times, compared to when the label is not present. This is despite having to use a silver isotope (^{107}Ag) that is not particularly rare (approx. 52% of the elements total natural abundance).

In the longer term, such labeling techniques could also be used to assign ownership of nanoparticles to particular manufacturers, thus contributing to future legislative traceability and accountability needs.

Uptake and internalisation

Imaging of nanomaterials within organisms is also helpful for understanding their environmental impacts. I have described evidence of the internalisation of silver nanoparticles by the polychaete *Nereis diversicolor* after feeding on sediment spiked with either nanoparticulate or aqueous silver (*10*). The study indicated direct internalisation of silver nanoparticles. Importantly, silver delivered in dissolved form was internalised via different routes than were silver nanoparticles, and the two types of silver preparations had different *in vivo* fates.

To establish mechanisms of uptake, we have used pharmacological inhibitors to block specific uptake pathways that have been implicated in the transport of metal nanoparticles and aqueous metal forms. This study, which focused on the mud snail *Peringia ulvae*, showed that nanoparticulate silver is taken up via multiple pathways and that these pathways are simultaneously active (*11*).

More recently, we have monitored in detail the cellular uptake of titania (TiO$_2$) nanoparticles into A549 (human epithelial) cells. This work demonstrated that the surface chemistry of nanomaterials plays a critical role in their cellular internalisation (**Figure 3**).
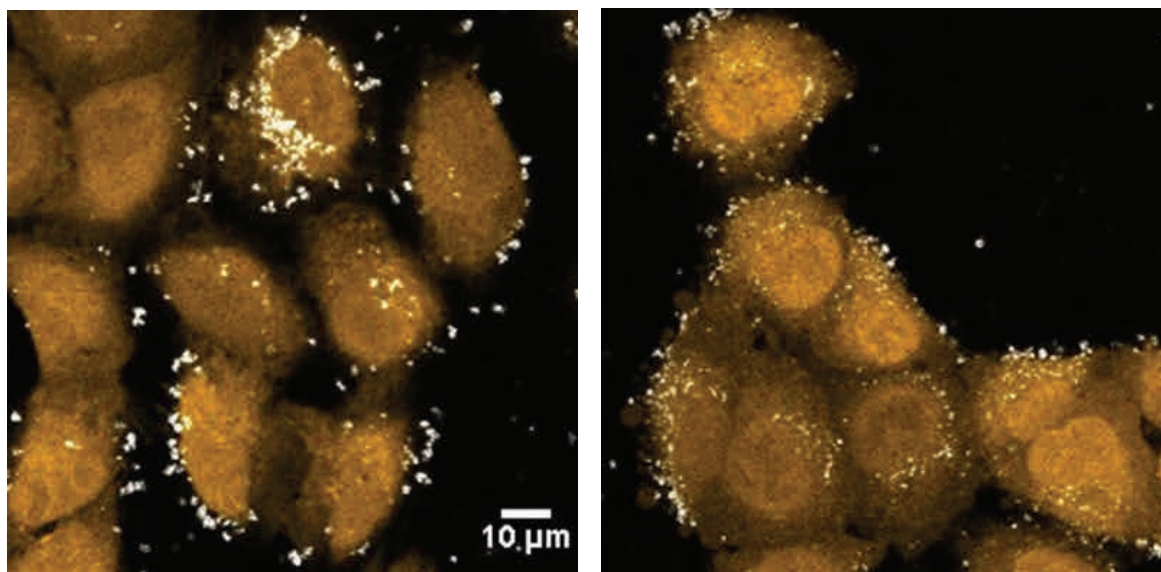
Figure 3. Confocal reflectance microscopy, showing the effect of surface modification on the uptake of titanium dioxide (titania) nanoparticles by A549 cells. Dispex-coated titania particles remain outside the cell (left) ,whereas PVP-coated titania nanoparticles are internalised. (right) Credit: Abdullah Khan, University of Birmingham

Outlook

A large body of recent work is contributing to a better understanding of the safety of nanomaterials. Acute toxicity effects discovered to date are generally limited. However, the quantitative data from experiments performed in realistic and environmentally/biologically relevant conditions remain too scarce to permit predictions of nanomaterial toxicity. A framework to enable the regulation of nanomaterials has yet to emerge.

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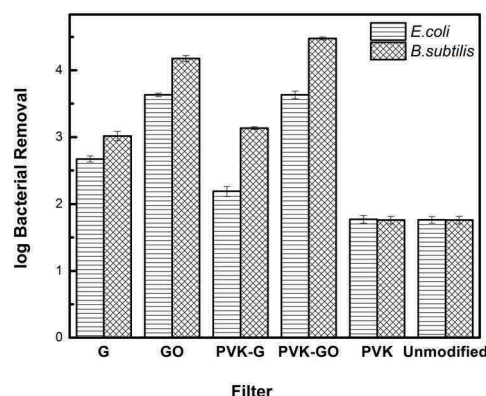
Article

Overcoming nanoecotoxicological effects for sustainable remediation of nanomaterials

Debora F. Rodrigues (University of Houston, dfrigirodrigues@uh.edu)

Graphene oxide is a promising material for water purification with its antimicrobial properties and high sorbing capacity for heavy metals. The *in vitro* toxicity profile of graphene oxide precludes its direct use in water treatment, but the combination of graphene oxide (and related nanomaterials) with polymers retains the metal adsorbent and antimicrobial properties, with the mitigation of possible toxic side effects.

Figure 1. *Log bacterial removal after filtration through nanocomposite membrane filter. Concentration of nanomaterial solution on filter: 1 mg/mL.*

The advancement of nanotechnology has led to the emergence of various types of metallic and carbon-based nanomaterials (*1, 2*). For example, graphene oxide (GO), a carbon-based nanomaterial, is a promising adsorbent for heavy metals (*3-6*). GO can adsorb significantly more heavy metals (Cu^{2+}, Cd^{2+}, Co^{2+}) from aqueous solutions than unmodified carbon nanotubes and activated carbon (*5, 7*). Heavy metal sequestration by GO occurs mainly through oxygen-containing functional groups, such as carboxyl (COOH) and hydroxyl (OH). The removal of heavy metals is highly dependent on the pH because these functional groups can undergo protonation or deprotonation, depending on the pH (*4, 8*).

GO has anti-microbial properties (*9, 10*), which makes it a potentially useful material for water treatment. Concentrations as low as 45 mg/L to 85 mg/L lead to levels of microbial inactivation between 59% and 74%, while higher concentrations result in 100% microbial inactivation (*10,11*). Although GO has superior anti-microbial properties and better heavy metal removal capacity than most commonly used drinking water adsorbents, *in vitro* toxicity tests currently preclude the use of GO in water treatment. Several cytotoxicity studies with GO nanomaterials report problematic effects on human and other mammalian cells. As

observed in antimicrobial studies, nanomaterial size, shape, dose, and exposure time were found to play an important role in their cytotoxic properties. In human cell lines, GO can generate reactive oxygen species (ROS) (*12*) and, depending on the human cell line, these nanomaterials can be toxic at concentrations varying from 50 mg/L (*13*) to 85 mg/L (*10*). However, when these nanomaterials are combined with biologically compatible polymers (e.g. PEGylation), they exhibit negligible *in vitro* toxicity to many cell lines, even at high concentrations up to 100 mg/L (*14, 15*). Similar results were observed in animal models (*13, 15*). Furthermore, it was found that small sizes of GO-PEG in the range of 10 to 50 nm showed no obvious toxic side effects on treated mice in 40 days (*16*). In fact, it was observed that the nanomaterials were gradually excreted by mice while causing no noticeable toxicity to the treated animals (*17*).

Overcoming toxicological effects

All previous studies showing toxicity of GO nanomaterials were carried out under pristine conditions. Recently, my research group determined the toxicity of a nanocomposite containing 30 mg/L of GO
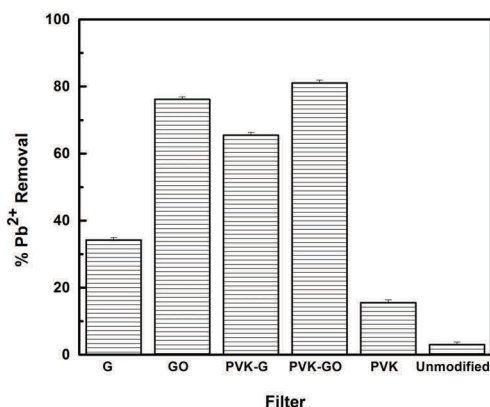
Figure 2. Percentage Pb²⁺ removal after passing through filters. Concentration of nanomaterial solution on filter: 1 mg/mL.

embedded in a biologically compatible polymer, poly(*N*-vinyl)carbazole (PVK), at a concentration of 970 mg/L (*18*). In this study, we showed that this nanocomposite achieved 80% more inactivation of *E. coli* than pure GO by increasing the dispersibility of GO in aqueous solution (*18*). These results indicated that it is possible to reduce the concentration of GO to levels that are non-toxic to humans and animals and at the same time maintain the antimicrobial properties of GO.

In a further step, to determine the potential application of this nanocomposite for water treatment purposes, my research group coated commercially available membrane filters with poly(*N*-vinylcarbazole) (PVK), graphene (G), graphene oxide (GO), poly(*N*-vinylcarbazole)–graphene (PVK-G), and poly(*N*-vinylcarbazole)–graphene oxide (PVK-GO).

The results demonstrated that graphene-based nanocomposite membrane filters had improved antibacterial activity and heavy metal removal capacity compared to unmodified membrane filters.

To estimate the effectiveness of the modified membrane filters to remove bacteria, bacterial plate counts were conducted in the filtrate, after filtration of bacterial solutions. The results depicted in **Figure 1** show that both GO and PVK-GO plate counts estimated 4 to 3 log removal for *B. subtilis* and *E. coli*, respectively. The amount of Pb²⁺ removed with the filter was also determined in the filtrate through atomic adsorption spectroscopy and reported as percentage Pb²⁺ removal (**Figure 2**). The results show that the PVK-GO modified membrane filter consistently exhibited the highest percentage Pb²⁺ removal, with 81.04%, followed by GO modified membrane filters, with 76.19% Pb²⁺ removal.

The other modified membrane filters, such as PVK-G, G, and PVK, could remove 65.51%, 34.21% and 15.53%, respectively.

Conclusion

The dispersion of graphene–based nanomaterials in concentrations that are non-toxic to humans on the surface of commercially available membrane filters can significantly improve the antibacterial property and heavy metal removal capacity of commercial membrane filters. Therefore, it is possible to immobilise nanomaterials in nanocomposite forms for applications in water treatment.

Acknowledgements

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Article

Are standard ecotoxicological bioassays a blessing or a curse?

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The need to manage the use of chemicals in a sustainable manner has led to the development of scientific and regulatory approaches for assessing prospective and retrospective risk. As an emerging area of industrial development that can have potential environmental impact, nanotechnology requires similar regulation. With the growing production of a wide array of nanomaterials with different sizes, compositions, surface coatings and other properties, there is concern that some of these nanomaterials may be toxic in ways that are not predictable based on bulk material properties. An initial challenge for the regulation of nanotechnology products is to assess which components of the current chemical risk assessment methods should be used with nanomaterials. Reliable methods are needed for studying how different nanomaterials may behave in natural systems and how they interact with living organisms.

Credit: kwanchai.c/Shutterstock

As it grows, the field of nano-ecotoxicology has been able to draw extensively on existing tools and techniques for assessing chemical risk. Within regulatory ecotoxicology, a key recognised requirement is to have standardised protocols available for toxicity testing. Such agreed protocols are vital because they ensure that studies conducted in different laboratories can be compared and can inform risk assessments for nanomaterial regulation under different jurisdictions. Standardised toxicity tests have also been developed to inform nanomaterial regulation. However, these standard test methods are often also used in more fundamental nanotoxicology research. Often these uses are entirely appropriate for the question under study. However, in other cases, limiting studies to standard species, test methods, and endpoints may lead researchers to miss key aspects and issues in eco-nanotoxicology that would be revealed by the use of nonstandard test systems. For example, a growing number of studies have assessed the responses of soil-dwelling species to nanomaterial exposure, recognising that soils are likely sinks for nanomaterials. These studies illustrate the importance of going beyond a standard set of species, soils, and endpoints to understand the toxicity effects of nanomaterials.

Selection of species for testing

Toxicity can rarely be examined for a wide range of species or at the ecosystem scale, except for the chemicals of highest environmental concern. To protect

ecosystem structure and function, risk assessment generally relies on data for a very limited number of (usually short-lived) species. To assess nanomaterial toxicity for soil ecosystems, the most commonly used test species are the earthworm *Eisenia fetida*, the springtail *Folsomia candida* and the nematode *Caenorhabditis elegans* (*1*, *2*, *3*). Standardised tests for these species have been available for over 10 years and are widely used in nano-ecotoxicology research. Of the 79 papers published on nanomaterial toxicity to soil organisms by June 2015, 64% studied just these three species (*E. fetida,* 28%; *F. candida,* 9%; *C. elegans,* 27%).

These studies have led to a number of insights. At least for metal and metal oxide nanomaterials made from silver, zinc oxide and copper oxide, nanomaterial toxicity is most frequently lower than the toxicity of the metallic component alone in ionic form. Indeed, meta-analyses by Notter *et al.* (*4*) revealed that nanomaterial toxicity was at or below ionic metal toxicity in 93.8%, 100% and 81% of paired studies for Ag, CuO and ZnO nanomaterials respectively. However, the focus on so few species limits the chance to identify unexpected effects in species that are rarely, if ever, used for study. On a more practical level, focus on just a few organisms makes it difficult to develop robust species sensitivity distributions. For certain metals and pesticides (e.g. zinc, chlorpyrifos), it has been possible to build robust species sensitivity distributions as an excellent basis from which to derived scientifically credible environmental quality standards (*5*, *6*). The current focus on using mainly standard test species may delay such comprehensive assessments for nanomaterials in soil.

> **Because standard tests encourage the use of a very limited number of species, many species and indeed whole phyla will rarely, if ever, be tested.**

Use of a standard test medium

One of the most important innovations to allow the standardisation of terrestrial toxicity tests has been the use of standard test soils. Natural (e.g. LUFA 2.2) and/or artificial soils have been proposed and used for this purpose. The deployment of the same media across tests provides a constant set of conditions that govern bioavailability for the same soil in different laboratories. However, the bioavailability and toxicity of metals are strongly affected by different soil properties, such as soil pH, organic matter content, clay content, cation exchange capacity, and iron oxide content. These soil properties may also affect how nanomaterials behave in soil. For example, the chemical composition of the nanomaterial, pH, organic matter content and soil clay composition can all affect nanomaterial uptake by organisms and the resulting toxic effects (*7*, *8*). For metals, key innovations such as the terrestrial biotic ligand model (*9*) provide a mechanistic framework for identifying major soil physiochemical drivers that influence nanomaterial toxicity; knowledge of these drivers can be used to support site specific risk assessments. To extrapolate nanomaterial toxicity observed in one soil type to another, there is an urgent need for the development of variants of these models. Such developments require data on toxicity in different soil types, not just standard tests with a single soil type.

Measurement endpoints

The classic endpoint measured in toxicity tests is mortality. However, this endpoint is a crude measure of possible ecological effect. In many standard tests for soil species, the capacity also exists to measure sublethal effects e.g. on reproduction, growth, and even multiple life cycle traits. Going beyond organism life cycles, there remains a dearth of studies of nanomaterial effects on genetic/epigenetic, physiological and behavioural properties of sensitive soil organisms. Recent studies on the effects of metal, pharmaceutical and pesticides have shown that these biological traits may be much more sensitive to chemical influence than are more classically assessed endpoints.

There is also some evidence that nanomaterials may differ from their ionic chemical counterparts in how they are taken up by organisms. Transcriptomic and biological imaging studies for soil organisms have suggested the possibility of active uptake of nanomaterials though cellular endocytosis pathways (*10*, *11*). This uptake mechanism leads to a higher overall accumulation of nanomaterials than for their metal constituents. The long-term physiological consequences of this "over-accumulation" of nanomaterials have not been fully established. It would benefit the field greatly to understand how these effects may underpin impacts on sensitive endpoints and the resulting long-term effects. This will require tests that go beyond durations routinely used in standard tests.

Long-term/transgenerational toxicity

Perhaps the greatest challenges for interpreting the effects of exposure to nanomaterials from current standardised toxicity tests is the relatively short-term nature of these assays. For many aquatic toxicity tests, the period of exposure is very short (48 or 96 hours).

For soil toxicity tests, exposure periods are often longer (e.g. 28 days). However, considering that an earthworm may be able to survive for up to 5 years, this is a relatively short exposure given the organism's lifespan. Furthermore, chemical and nanomaterial interactions with the different components of the epigenome may affect to what extent toxic effects are transferred to subsequent unexposed generations (*12*). Further, a recent study conducted in our laboratory with the nematode *C. elegans* has shown that long-term multi-generational exposure results sensitises subsequent generations to silver nanoparticles (and also silver ions), and that this sensitisation is retained even if exposure is removed for five generations. Thus, although short-term tests may be ideal for identifying acute toxicity, new approaches will be needed to understand complex, long-term effects.

Outlook

Given the expected increase in nanotechnology product use, we will become more reliant than ever on the availability of robust risk assessment scheme to help balance risks and benefits of these novel materials. Work conducted to date has shown that key methods for chemical fate modelling, toxicity testing, and biological endpoint assessment are often fit for purpose for applications in regulatory nanomaterial assessments. Existing standardised toxicity tests provide tractable and useable tools for the rapid generation of initial toxicity data that are comparable between laboratories, with only a few modifications needed for their use with nanomaterials. Although valuable for routine studies, standard tests are, however, not a panacea for all cases. Because standard tests encourage the use of a very limited number of species, many species, and indeed whole phyla, will rarely if ever be tested. This raises the real possibility that vulnerable species are, and will continue, to be missed. Further, it is difficult to know just how relevant short-term data in a single standard test medium are for different environments, over extended exposure times, and for all species in exposed communities.

When considering the use of standard tests for nano-ecotoxicology, the words of Sumpter and Johnson (*13*) on the lesson learned from studies of endocrine disrupting chemicals in the aquatic environment should be borne in mind. They concluded: "One lesson ... during the 10 years of research on endocrine disruption is that the current testing regime used to determine the toxicity of a chemical to aquatic organisms has "failed", in the sense that it has not detected the endocrine activity of many chemicals" and that "even more surprisingly, it transpired that EE2 [ethinyl estradiol, a potent endocrine disrupting chemical] is acutely toxic to fish, but this effect is delayed long enough that it is not detected in the acute toxicity test protocols used currently." These comments suggest that we should be careful as scientists not to overly rely on standard tests for ecologically meaningful risk assessment of nanomaterials released into the environment.

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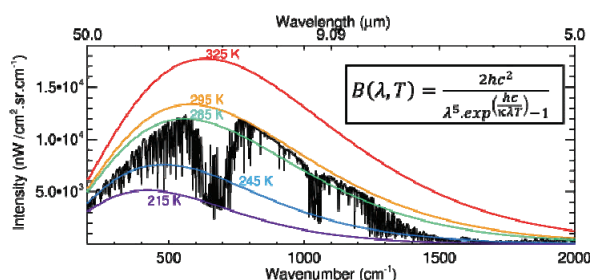
ECG Environmental Briefs   **(ECGEB No 10)**

Thermal infrared remote sensing of the atmosphere

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Thermal infrared (TIR, 200 to 2000 cm^{-1}) sensors on satellites provide global and diurnal measurements of the Earth's top-of-the-atmosphere (TOA) radiation. These sensors are most sensitive to the mid- and upper tropospheric regions of the atmosphere, where monitoring of greenhouse gases and pollution plumes has become increasingly important. This Brief describes how thermal infrared radiation can be used to determine atmospheric concentrations from space.

Figure 1. *Intensity of the Planck radiation spectrum, B (λ,T), for a range of terrestrial temperatures (coloured lines) and a simulation of a typical atmospheric spectrum (black line). In Planck's law (top right), κ is Boltzmann's constant, h the Planck's constant, and c the speed of light.*

The spectral distribution of Earth's thermal radiation is governed by Planck's law, which describes the intensity of radiation, $B(\lambda,T)$, emitted by a black body (a perfect absorber and emitter of radiation) in thermal equilibrium as a function of wavelength (λ) and temperature (T). For a given temperature, the peak intensity of radiation for each Planck function is related to a particular wavenumber (coloured lines in **Figure 1**) (*1*). In reality, different types of surfaces, such as land, ocean, and snow, do not emit and absorb radiation efficiently: they are not perfect black bodies. This property is described by the emissivity (ε), the ratio of the radiation emitted by an object to the radiation that it would emit if it were a perfect emitter/absorber. A typical Earth spectrum, with a particular surface temperature and emissivity, observed from a TIR space sensor would therefore look like the black line in **Figure 1**. This spectrum is not smooth like the Planck curves, but rather exhibits a series of absorption lines and features. These lines contain the spectral fingerprint of many molecular species in the atmosphere. The region from 800 cm^{-1} to 1000 cm^{-1} is often called the "atmospheric window", where the atmosphere appears transparent. This region can be used to gain information on the Earth's surface, clouds and aerosols (*2*).

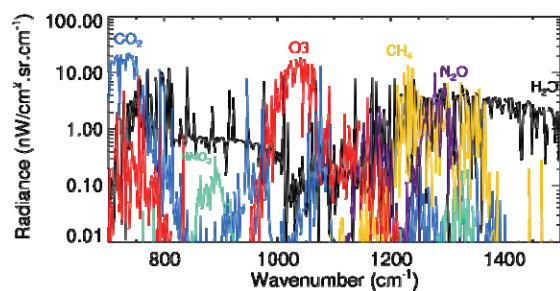**Figure 2** shows how different atmospheric species contribute to the radiation intensity observed in a TIR spectrum. Some species such as ozone (O_3) and methane (CH_4) have strong spectral bands. Other species like carbon dioxide (CO_2) and water vapour (H_2O) have a broader series of spectral lines (or "continuum" spectra) present throughout most of the TIR spectral region.

The intensity of TIR radiation and the type of feature observed in a TIR spectrum is dictated by a number of processes. Firstly, absorption (or emission) spectral lines are only produced when a photon is absorbed (or emitted), creating a transition of energy states on a molecular level (*3, 4*). In the TIR region, such spectral lines correspond to particular molecular transitions that are described as rotational, vibrational or simultaneous rotational-vibrational (*5*). Secondly, photons can only be absorbed to produce vibrational or rotational transitions if the charge around the molecules is separated so as to produce a permanent electric dipole. Thus, the geometry of the molecules and the abundance of the species in the atmosphere affect the type of spectral feature observed. Now that we recognise what a TIR spectrum looks like, how can we relate interactions between molecules and TIR radiation to the radiation detected by a space-borne sensor?

Radiative transfer

Imagine a beam of radiation travelling through a small section of air. The air is made up of changing

Figure 2. TIR contribution of a range of atmospheric species. The species labels are colour-coded to match the spectral features for each species.

concentrations of different species, with all molecules absorbing and emitting thermal radiation at different rates. As the radiation travels through different layers of the atmosphere, the intensity of radiation will constantly be modified by both absorption and emission processes, as given by

$$\delta I = \delta I_{absorption} + \delta I_{emission}$$

where δI is a net change in radiation. This equation is a simplification of the *Schwarzschild's Equation*, which tells us how radiation changes through its travelled path due to all of simultaneous absorption and emission processes. Now imagine that this radiation is detected by a TIR sensor, such as a Fourier Transform Spectrometer (*6*), looking down at the Earth along a particular line of sight. The net radiation measured by the satellite sensor would be that which is attenuated through each layer (as small increments of absorption and emission) from the surface to the top of the atmosphere *plus* the radiation emitted directly from the surface. In this case, this process can be described by the radiative transfer equation (RTE):

$$I(sensor) = I(surface) + I(atmosphere)$$

In remote sensing, I is usually called the radiance (with units W sr^{-2} m^{-2}). The equation is shown here for a very simplistic scenario. In reality the atmosphere is highly scattering (an effect often assumed to be negligible in the TIR unless clouds and aerosols are present). In these cases, the RTE becomes much more complex to account for additional processes affecting the radiation (*1*).

Retrieving atmospheric species

In practice, information about an atmospheric species is *retrieved* using a computer algorithm to solve the RTE. The algorithms use an inversion technique, i.e. they mathematically invert a TOA satellite radiance measurement to infer the atmospheric state.

The problem of solving the RTE to determine an atmospheric concentration is imperfectly defined, because the satellite measurement only provides a snapshot of information about the atmosphere and we must make assumptions about the atmospheric and surface state for that time. There is thus no unique solution, and only the most probable solution can be determined within some uncertainty range (*7*). Generally, for TIR atmospheric retrievals, an optimal estimation (OE) technique is employed. A typical OE retrieval algorithm requires calibrated spectra from a satellite measurement (covering the spectral range which has the largest sensitivity to the target species); once spectra are extracted, suitable prior data are selected. The prior data are used to simulate (with a radiative transfer model) the satellite measurement and when a good simulation is obtained, the algorithm will solve relevant equations to extract the target species and an uncertainty estimate.

For the retrieval to be as accurate as possible, the prior data (i.e. vertical profiles of temperature and pressure, the target species, any interfering species, surface temperature and emissivity) should match the measurement time and location as closely as possible. The simulation must incorporate up-to-date spectroscopic line and cross section information. A poor representation of prior data, spectral lines and cross sections will result in an inadequate simulation compromising the accuracy of the retrieved quantity. For specific examples of remote sensing of different tropospheric species in the Earth's atmosphere see (*8*).

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Biotic ligand models, metal bioavaila-bility and regulatory application

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Biotic ligand models are tools used to predict the trace metal concentration in the water column that will have an adverse effect upon an aquatic organism. This Environmental Brief outlines how biotic ligand models have been developed, and how they are now being applied to set and implement regulatory quality standards.

The ecotoxicity of many trace metals to aquatic organisms depends on water chemistry conditions. This has been taken into account during the setting of environmental quality standards for metals in the past, predominantly through the use of water hardness-based corrections. These water hardness corrections were based on the observation that metal toxicity was generally lower at high hardness than at low hardness in laboratory ecotoxicity tests. Regions with soft waters were identified as being particularly sensitive to trace metal toxicity and so where assigned relatively low environmental quality standards.

Fish gills were identified as the site of metal uptake causing toxicity, and experiments led to the development of the Gill Site Interaction Model (*1*) which relates the level of toxicity to the degree of accumulation of metal on the gill surface. If the binding constant for metal at the fish gill is known then the degree of metal accumulation at the gill can be related directly to the free ion activity in the water that the gill is exposed to. This model also resulted in the calculation of stability constants for metal binding to fish gills. The competitive effect of the hardness cations Ca^{2+} and Mg^{2+} on metal toxicity could then be interpreted in terms of their competition with divalent trace metals binding to ligand sites on the fish gills.

Another factor in defining the toxicity of a metal is the degree of binding to dissolved organic carbon (DOC)

such as humic and fulvic acids, because the metal-organic complexes do not contribute directly to the organism toxicity. Advances in chemical speciation modelling were provided by models, such as the Windermere Humic Aqueous Model or WHAM (*2*), which are able to describe the interactions between trace metals and humic and fulvic acids in natural waters. These models enabled the free ion activities of metals in natural waters to be predicted, and where comparisons with direct measurements of free ion activities were possible there was typically good agreement (*3*).

A further key development in the understanding of trace metal toxicity was achieved through combining both the Gill Site Interaction Model with the aqueous speciation model WHAM to produce the Biotic Ligand Model (BLM) (*4*). This model treated the metal binding sites present on the fish gills as an additional ligand in the chemical speciation model, and enabled the equilibrium speciation of metal between gill ligands, DOC, solution complexes, and the free ion activity of the metal to be predicted. This

SCHEMATIC OF BIOTIC LIGAND MODEL
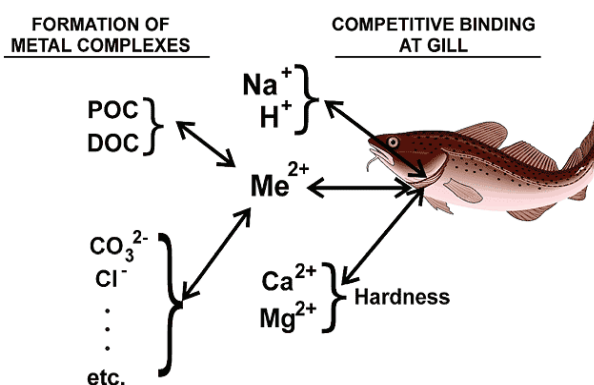
Figure 1. Schematic of the biotic ligand model, showing the chemistry speciation component on the left and biological interactions on the right. Me^{2+} represents a divalent metal ion. POC is particulate organic carbon; DOC is dissolved organic carbon. Adapted from (4).

development provided the first direct link between the dissolved concentration of a metal, as is measureable in filtered samples by routine analytical methods, and the level of toxicity experienced by an organism in complex natural waters.

The BLM considers the inorganic speciation reactions of the metal and system components, and the binding of cationic species to both DOC (usually assumed to be present as fulvic acid only) and the "Biotic Ligand", which is an assumed metal binding site on the animals gills (or some other exposed membrane surface). This concept is shown schematically in **Figure 1**. The interactions between a trace metal and cations in the bulk solution, such as H^+, Na^+, Ca^{2+} and Mg^{2+}, are much more complex than is predicted by the hardness-based metal standards historically used, because all the cations interact competitively at the binding sites on both the DOC in solution and the biotic ligand on the organism. Therefore, a solution based measurement of either the free ion activity or some other "available" fraction, is unable to completely replicate the sensitivity of the organisms to changes in the water chemistry.

Does the biotic ligand model work?

Validation studies have shown that the bioavailability models which have been developed for specific species can be applied to understand the effects of bioavailability on other species from the same trophic level (*5*). The extrapolation of the BLMs between different species requires a bioavailability correction to be made for each individual species within a species sensitivity distribution (SSD) (or even each individual toxicity endpoint within the database) to the same specific set of water chemistry conditions (*6*). This correction allows the relative sensitivity of different organisms to be compared under conditions for which they have not necessarily been tested.

The calculation of a site-specific bioavailability normalised SSD requires a water quality standard, which may be derived from data for a particular set of water chemistry conditions, to be corrected for the local water chemistry conditions at each site. This site-specific standards result in calculated dissolved metal concentrations against which compliance can be assessed by routine regulatory monitoring, provided that the required supporting parameters which are required for the bioavailability normalisation are available.

Within Europe, the development of bioavailability based environmental quality standards for metals has followed this type of approach, using an SSD of chronic ecotoxicity data which is normalised to different water chemistry conditions using a suite of BLMs developed for different trophic levels. The BLM normalised SSD is then calculated for a diverse range of European water chemistries in order to identify the most sensitive water chemistry conditions which are likely to be encountered. The environmental quality standard is expressed as a "bioavailable metal" concentration, which ensures a high level (e.g. 95%) of protection in regions with sensitive waters (i.e. where bioavailability is maximised). Exposure monitoring data for dissolved metal can be converted into a "bioavailable metal" concentration using the BLM for comparison against the environmental quality standard. This approach allows the environmental quality standard to be expressed as a single value (for example across the whole of Europe), whilst also enabling it to be corrected to local conditions and ensuring a consistent level of acceptable potential risk.

In practice, the available regulatory monitoring data do not tend to include measurements of dissolved organic carbon, which are required for the BLM calculations, although pH is commonly measured. This omission occurs because water hardness has historically been required in most cases. It is possible to estimate the concentrations of other major ions in solution from the concentration of calcium or other parameters (*7*) with sufficient precision to allow robust BLM calculations. The routine regulatory use of BLMs marks a step change in the way water quality is assessed and delivers a clear evidence-driven link to environmental protection.

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