

## February 2018

# ECG *Bulletin*



**Environmental Antibiotic Resistance.** This edition features an article by Roger Reeve on the chemistry and microbiology of environmental antibiotic resistance (*pp.17-20*), followed by details of our 2018 Distinguished Guest Lecture (*pp. 21-22*), hosting Professor Joakim Larsson, University of Gothenburg.

**Chair's Report.** Zoë Fleming reflects on our new website, outreach, scientific meetings, and committee changes that have taken place across 2017.

**Environmental Briefs.** Luke Beesley provides insight into modified bio-sorbents in heavy metal contaminated

soil (*pp. 23-24*); Stephen Lofts models the influence of speciation on metal behaviour and toxicity (*pp. 25-26*); and Laura Newsome explores the (bio) geochemistry of radioactive substances (*pp. 27-28*).

**Also in this issue.** Valerio Ferracci tells us about his sensor work (*p. 4*); and, with Rupert Purchase, reviews two new books (*pp. 5-7*); Tom Sizmur and Laura Newsome provide meeting reports on soil organic matter (*p. 9*) and geochemistry (*pp. 10-11*); and articles cover emerging organic contaminants (*pp. 12-13*), and water-based chlorine disinfection (*pp. 14-16*).

# Contents

<b>Chair's Report:</b> <i>Zoë Fleming</i>	3
<b>ECG Interview:</b> Valerio Ferracci	4
<b>Book Review,</b> by Valerio Ferracci	5
<b>Book Review,</b> by Rupert Purchase	6
<b>Meeting Report:</b> Environmental Chemistry of Water, Sediment Soil and Air, by Brian Graham	8
<b>Meeting Report:</b> 6th International Symposium on Soil Organic Matter, by Tom Sizmur	9
<b>Meeting Report:</b> 27th V. M. Goldschmidt Conference, Paris, 14th – 18th August 2017, by Laura Newsome	10
<b>Article:</b> Emerging organic contaminants, by Jamie Harrower	12
<b>Article:</b> Chlorine-based water disinfection, by Glynn Skerratt	14
<b>Article:</b> Antibiotic resistance – antibiotic release into the environment, by Roger Reeve	17
<b>Upcoming Meeting:</b> Biopollution: Antimicrobial Resistance in the Environment	21
<b>ECG Environmental Brief:</b> The application of modified bio-sorbents to heavy metal[loid] contaminated soils, by Luke Beesley	23
<b>ECG Environmental Brief:</b> Modelling metal speciation in natural waters, by Stephen Lofts	25
<b>ECG Environmental Brief:</b> Geochemistry and biogeochemistry of radioactive substances, by Laura Newsome	27



*Cover image: The last tree to survive urbanization, Credit: Giordano Aita/Shutterstock*

## ECG Bulletin

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## Report

# Chair's report for 2017

Zoë Fleming (NCAS, University of Leicester)

During 2017, the Environmental Chemistry Group Committee organised a number of successful meetings, events and activities across a range of topics and formats.

With five new recruits to the committee, we are working on several new ideas and projects, and have benefited from this influx, updating the way we communicate with our members. We recruited two interns under the guidance of Dr Laura Newsome of the University of Manchester who designed and populated our **new website** with the last ten years of ECG *Bulletin* articles. We hope this resource will be useful for you all as it allows each article to be searchable and independent of the *Bulletin* edition it was published in.

Our first event of the year was the 2017 **Distinguished Guest Lecture** and Symposium on 1st March, on the topic of air quality and emissions from transport: **"Inside the Engine: from Chemistry to Human Health"**. Dr Clare Holman of Brook Cottage Consultants provided the introduction to the seminar, speaking on the links between diesel and air quality, vehicle regulations and general emissions legislation. This was followed by Dr Jacqueline Halmilton from the University of York introducing the analytical techniques for identifying pollutants, and Simon Birkett (Director of Clean Air in London) discussing the history of favouring diesel based on CO<sub>2</sub> targets. The Distinguished Guest Lecture was delivered by Professor Frank Kelly of King's College London, who spoke on the symposium title. Detailed reports from the meeting can be found in the July 2017 edition of the ECG *Bulletin* and on our new website.

This event was closely followed by a meeting entitled **"What's new in the analysis of complex environmental matrices"** run by Dr Roger Reeve (University of Sunderland). These meetings have run every 2 years so we look forward to planning the next for March 2019.

The ECG **outreach activities** are growing from strength to strength. Dr Zoë Fleming (University of Leicester) and Dr Rowena Fletcher-Wood (Science Oxford) brought together 12 other volunteers to work on a 4 day public outreach event (**Unearthed — explore the world at your feet**) in Edinburgh at Dynamic Earth, celebrating and showcasing NERC science. The group has a suite of hands-on activities involving air, water and soil pollution, so please contact us if you hear about an event where they would be well received, or if you would like to volunteer

with us.

Dr Tom Sizmur (University of Reading) organised an **Early careers meeting** on the **Environmental Chemistry of Water, Sediment, Soil and Air** at Burlington House on December 14th for the second year running. This event attracted 44 delegates, 2 invited speakers and talks and posters with prizes for the best of each category.

Alongside our programme of events, ECG Committee members Dr Julia Fahrenkamp-Uppenbrink, Dr Rowena Fletcher-Wood, Dr Tom Sizmur, Dr Rupert Purchase and Dr Roger Reeve have continued to produce the biannual **ECG Bulletin**, with involvement from Dr Glynn Skerratt, Dr Valerio Ferracci, and Dr Clare Topping in the latest issue. Professor Martin King (Royal Holloway) has been active in the further development of the **ECG Environmental Briefs**, a series of short documents giving a brief but precise introduction to topics of relevance to environmental chemistry. We now have 17 Environmental Briefs (all available on the website) and 2 Early Career Briefs (written by students and edited by the committee).

Forthcoming events in preparation for 2018 include a joint meeting with the Mineralogical Society in June, as well as joint meetings with the Water Science Forum and Toxicology groups. The **2018 Distinguished Guest Lecture** titled **"Biopollution: Antimicrobial Resistance in the Environment"** will be held on 28th March at Burlington House with Joaquim Larssen from the University of Gothenburg as the Distinguished Guest Lecturer. We will be reaching out to ECG members in early 2018 to ask about what Continued Professional Development (CPD) activities would be useful for you.

We will have 5 members leaving the committee in March 2018 and would like to especially thank Bill Bloss (University of Birmingham) who has served for ten years and Rupert Purchase who has served on the committee since 1986 and co-edited the first *Bulletin* in 1995. We would also like to thank Julia Fahrenkamp-Uppenbrink (Science) for her work on the *Bulletin* since 2011.

At 1,833 members, we are one of the largest interest groups. The committee is always keen to hear your feedback on events and suggestions for future events. I would like to thank the committee and those who have participated in the diverse activities of ECG for their enthusiasm and for volunteering their time.

# The ECG Interview: Valerio Ferracci

Valerio Ferracci is a Research Fellow in the School of Water, Energy and Environment at Cranfield University, specialising in field measurements of trace species in the atmosphere.

## What inspired you to become a scientist?

I have always enjoyed puzzles, and science, to me, offered a very similar intellectual stimulus. Having said that, I did have a genuine interest in most subjects at school and, as a result, found the choice of an undergraduate degree course quite daunting. In the end, chemistry won over fierce competition from the humanities: it draws on so many other fields (from physics and maths to, I dare say, philosophy!) that it effectively feels like working in multiple disciplines.

## How did you come to specialise in atmospheric chemistry?

During the first years of my undergraduate degree, I was pretty set on inorganic chemistry, but a simple computational practical on simulating the vertical distribution of atmospheric ozone changed all that. The way in which some relatively simple yet elegant reaction kinetics (the Chapman cycle, etc.) could account for the existence of the ozone layer in the stratosphere really struck a chord with me. I then undertook a summer internship, a Masters project and a PhD, all in atmospheric chemistry. Focusing on atmospheric ozone at the beginning of my career was also very inspiring, as it offered a compelling narrative both on the detrimental impacts of human activities on the planet, and on what the rapid, concerted remedial action of science and policy can achieve.

## Could you describe your current job?

My main interest at the moment is in the use of relatively low-cost sensors to underpin emissions of atmospheric trace species, from greenhouse gases to urban pollutants and biogenic volatile organic compounds. These instruments have the potential to improve on both the spatial and temporal coverage of techniques currently used in atmospheric science, helping with regional air quality to global emissions inventories. The job itself is rather varied: it involves time in the lab developing and

testing the sensors, field deployments in a variety of environments (from urban areas to remote forests), and plenty of data analysis.

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

I can't stress enough the interdisciplinary nature of environmental science. Keep up to date with what's current in a variety of fields, even if they feel unrelated to your research. If you can, pick up computer programming early on in your career: it is definitely not "just for modellers", and being fluent in one or two languages will be an invaluable skill in all sorts of situations.



Photo courtesy of Tomás Sherwen

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

Communicating to disengaged, sceptical or misinformed audiences is very relevant to environmental scientists in this day and age. I do not think that there is an easy solution: encouraging scientists to engage with the general public is a good start, as well as trying to help people discern the difference between opinions and scientific consensus.

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

I found the variety associated with atmospheric science most rewarding. I was fortunate to work in a laboratory on gas radical kinetics, run global chemistry-climate models on supercomputers, and even fly on a research aircraft. Most definitely no two days are the same.

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

I would like to think it would be something yoga-related. I have come to appreciate the physical awareness that comes with this discipline, so I would find integrating that in my professional life very appealing.

## And what do you do when you are not working?

Come rain or shine, you can find me walking my dog. He's a beagle, and his nose can compete with some of our most sophisticated gas sensors. I am sure there is a research proposal there somewhere...



**Book Review**

# Environmental Impact of Road Vehicles: Past, Present and Future

Valerio Ferracci (Cranfield University)

The 44th volume in the series on Issues in Environmental Science and Technology focuses on pollution from road transport, discussing its impact on air, water and soil. This topical analysis not only accounts for the “usual suspects”, but also highlights some of the less obvious consequences of road pollution.

Recent media coverage in the wake of the vehicle emission testing scandal and reports of poor air quality across the UK, particularly in London, have drawn renewed attention to pollution from road transport. Last year, the Environmental Chemistry Group hosted a one-day symposium (“Inside the Engine”, see ECG Bulletin, July 2017 <https://www.envchemgroup.com/2017-inside-the-engine.html>) illustrating the main environmental issues arising from road pollution as well as its detrimental effects on human health.

This book, organised in nine self-contained chapters and freely available as an e-book to RSC members at <http://pubs.rsc.org/en/content/ebook/978-1-78262-892-7>, provides an account of the

complexity of this environmental issue. It first focuses on the two main vehicle technologies currently used (petrol and diesel), and their atmospheric implications in terms of greenhouse gas emissions (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) and urban air quality (nitrogen oxides, ozone, particulate matter). It then expands on the impact of these vehicles on the environments beside roads, with a very clear description of the wash-off of pollutants from roads caused by rain, the subsequent contamination of soils and waters and the potential uptake of toxic substances (e.g. trace metals) by plants. Later chapters in the book focus on the development and assessment of alternative technologies to fossil fuels.

A recurring theme throughout the book is the importance of life cycle analysis for all vehicle technologies, old and new. A number of examples are

provided to illustrate how the assessment of the environmental impact of vehicles would be incomplete without taking into account both direct (e.g. tailpipe emissions) and indirect (e.g. fuel extraction, vehicle disposal) processes. The importance of this “well-to-wheel” analysis is evident when comparing alternative technologies with fossil fuels; in the case of biofuels, any reduction in CO<sub>2</sub> resulting from not burning fossil fuels may be partially offset by excess emissions of other powerful greenhouse gases (methane and N<sub>2</sub>O) from growing crops to produce biofuels. This type of assessment is even more critical for battery-powered electric vehicles, as the environmental benefits depend crucially on how electricity is generated.

The chapter covering the impact of noise from road transport on human health was most interesting to me: this area is not as well-studied as other aspects of road pollution, and suffers from the absence of a “noise observation” network akin to those for local air quality. Nonetheless, current evidence seems to indicate that traffic noise may play a role in the development of hypertension and ischemic heart disease.

## Food for thought abounds in the future scenarios described in the book

Food for thought abounds in the future scenarios described in the book: for instance, as electric vehicles are projected to become more widespread in the near future, new challenges will emerge

in recycling large numbers of lithium-ion batteries when these vehicles arrive at the end of their life cycles. At the same time, particulate matter from tyre and brake wear-and-tear will still be an environmental issue regardless of the fuel used to power vehicles. It is evident that, even when our dependence on fossil fuels for transport is a distant memory, our efforts in safeguarding the environment will be far from over.

*Environmental Impacts of Road Vehicles: Past, Present and Future; Issues in Environmental Science and Technology, Vol. 44*, edited by R. E. Hester and R. M. Harrison, Royal Society of Chemistry, Cambridge, 2017, pp xvi + 248. ISBN: 978-1-78262-892-7, DOI: 10.1039/9781788010221

## Book Review

# Ecotoxicology and Chemistry Applications in Environmental Management

Rupert Purchase (Haywards Heath)

The author of this textbook, the ecologist and environmental chemist Sven Erik Jørgensen (1934–2016), made many notable contributions to ecology and ecological modelling and management. In two influential books, *Fundamentals of Ecological Modelling* (4th edition, 2011) and *Towards a Thermodynamic Theory for Ecological Systems* (2004), Jørgensen and co-authors outlined the roles of mathematics and physical chemistry in understanding ecosystems and the impact of toxicants on the environment. Jørgensen had editorial responsibilities for the journals *Ecological Complexity* and *Ecological Monitoring*, and was editor in chief for *Encyclopedia of Ecology* (2008).

*Ecotoxicology and Chemistry Applications in Environmental Management*, written when the author was Emeritus Professor in Environmental Chemistry at the University of Copenhagen, is therefore a distillation of Jørgensen's work in ecology and environmental management. In chapter one, Jørgensen emphasises a holistic approach in understanding changes to ecosystems whether natural or anthropogenic in origin, and suggests seven management steps for integrated ecological and environmental management:

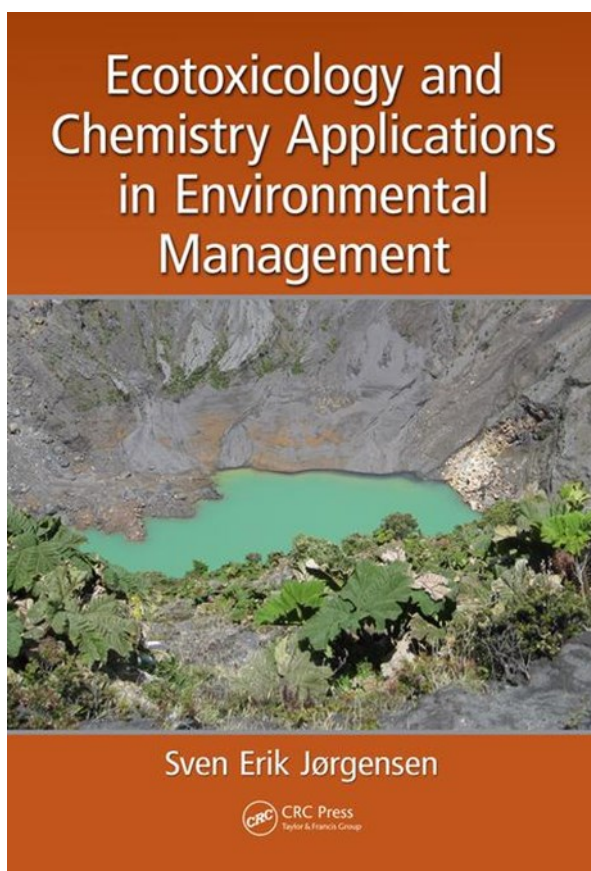
1. Define the problem.
2. Determine the ecosystems involved.

3. Find and quantify all the sources of the problem.
4. Set up a diagnosis to understand the relation between the problem and the sources.
5. Determine all the tools needed to implement and solve the problem.
6. Implement and integrate the selected solutions.
7. Follow the recovery process.

In the subsequent 14 chapters, Jørgensen characterises the properties and nature of pollutants, tools for modelling their environmental impact, and reviews some technological and societal solutions for environmental management. The longest chapter in the book concerns

**This book is highly recommended for students of environmental chemistry and should be available on the bookshelves of environmental managers.**

the application of the concepts of physical chemistry (essentially Gibbs' thermodynamics) to understanding the distribution of anthropogenic chemicals in the environment. The author estimates that hundreds of thousands of chemicals participate in environmental chemistry. Their chemical properties determine their distribution in the lithosphere, hydrosphere, atmosphere, and technosphere (the technologically modified environment), and hence the environmental and health effects of these substances. Jørgensen explains the concepts of acid-base equilibria, buffer capacity, metal-ligand complex formation and stability constants, the application of Henry's law for determining distribution between the atmosphere and hydrosphere, absorption isotherms, and redox chemistry. The author also provides fourteen worked examples to illustrate the application of these concepts. For example, how to calculate: (a) the  $[\text{Ca}^{2+}]$  and  $[\text{CO}_3^{2-}]$  content of an open freshwater system in equilibrium with solid calcium carbonate and with carbon dioxide at a defined pressure; (b) the concentration of the hydroxo species  $\text{Hg}(\text{OH})^+$  and  $\text{Hg}(\text{OH})_2$  in a lake of known total mercury concentration and pH.



**Figure 1.** *Ecotoxicity and Chemistry Applications in Environmental Management* – book jacket provided by CRC press.

In a chapter on the ‘Application of ecological models in environmental chemistry and ecotoxicology’, Jørgensen gives a lucid account of the construction and application of modelling in ecological and environmental management:

1. ‘Models are synthesis of all what we know – observations, theoretical knowledge, knowledge about rates and sizes, knowledge about food items etc.
2. Models are tools to overview complex systems.
3. Models make it possible to quantify by the use of mathematical formulations and computers.’

In a succeeding chapter on ecosystem health assessment (EHA), the author suggests that EHA and ecological monitoring are complementary tools in environmental management, and describes the criteria for the selection of ecological indicators for EHA and the classification of ecosystem health indicators.

The remaining chapters concern the application of engineering techniques in solving pollution problems. Three applications are distinguished:

1. Environmental engineering technologies (e.g. techniques for wastewater treatment).
2. The concept of ecological engineering – based on the work of US ecologist H. T. Odum (1924–2002) – for remediation, e.g. the construction of wetlands for the treatment of wastewater or diffuse pollution sources.
3. ‘Cleaner production’ techniques in environmental management. This area covers environmental auditing and environmental management systems, cleaner production techniques to reduce pollution and energy use, and ‘Green Chemistry’.

In the concluding chapter, Jørgensen returns to the seven steps he proposed for environmental management at the start, suggesting that the application of techniques developed over the past 45 years, and expertly reviewed in this book, allows each of these steps to be accomplished. Tools at our disposal allow us to:

1. Identify the environmental problem both qualitatively and quantitatively.
2. Develop a diagnosis that relates the environmental problem and its effects and consequences.
3. Combine several toolboxes that offer solutions to the problem, to suggest a proper ecological-economical solution.

This book is highly recommended for students of environmental chemistry and should be available on the bookshelves of environmental managers. A more comprehensive Subject Index (and an Author Index) would have been welcome.

Sven Erik Jørgensen, *Ecotoxicology and Chemistry Applications in Environmental Management*, CRC Press, Boca Raton, FL, 2016, xiii + 304 pp. Part of a series of monographs, ‘Applied Ecology and Environmental Management’, Series Editors Sven Erik Jørgensen et al.; <https://www.crcpress.com/Applied-Ecology-and-Environmental-Management/book-series/CRCAPPECOENV>; accessed 25 November 2017. ISBN 9781498716529

Please look out for forthcoming book reviews by ECG committee members, which will be published both in our biannual *Bulletin* and online, at <https://www.envchemgroup.com/reviews.html>.

If you would like us to review a particular book, please get in touch with a member of the committee.

## Meeting Report

# Environmental Chemistry of Water, Sediment, Soil and Air: Early careers meeting

**Brian Graham (National House Building Council)**

A group of 39 early career researchers gathered on 14th December 2017 at Burlington House, London to discuss issues relating to the environmental chemistry of water, sediment, soil and air.

The meeting was introduced by the meeting organiser, Dr Tom Sizmur of Reading University, swiftly followed by the first presentation by Camille Peers de Nieuwburgh of Imperial College London, which was on the characterisation of chemical signatures of water associated with hydraulic fracking. She characterised water produced from fracking and related activities and showed that these waters are more likely to be contaminated by the intrusive operations than from natural sources. The next presentation by Erin Losty of Cranfield University was on mixtures of disinfection by-products in drinking water, their toxicity and minimisation. Her talk explained issues surrounding the production of unwanted disinfection by-products, principally highlighting trihalomethanes and haloacetic acids. While many products are known about (circa 600), only a small number are regulated or measured.

The next presentation was a keynote talk from Dr Ailsa Stroud from the DEFRA Air Quality team. Ailsa talked about her work in policy areas such as sea level change, geoengineering, climate change, and air quality. She also talked about her career so far, including a PhD at the University of Cambridge, working at the British Antarctic Survey, and the opportunities that her air quality work has given her (including monitoring air quality at the top of the BT Tower). Before lunch, Ailsa presented the award for the best poster to Sarah Donoghue from Edinburgh University, who had produced a poster on the distribution of lead in soils of the greater Glasgow area.

After lunch, Tullus Bergmann from Queen Mary University of London presented research on quantifying mining legacy stocks within sediment deposits in a stream in Cornwall. His work looked at metals in the

sediment and explored the possible issues were it to remobilise. Collins Gameli Hodoli from Cranfield University then talked about automatic air monitoring devices in Ghana. His research looked at developing and using low cost sensors to analyse air pollutants such as NO, NO<sub>2</sub>, CO and VOCs as well as PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>.

A presentation followed from Sarah Chandler from the University of Brighton, who talked about the use of standalone reagentless sensors for metal analysis in marine environments. Her work is focusing on the development of an arsenic sensor which is accurate and low cost. Dmitriy Berillo from University of Brighton then talked about the use of cryogels-embedded bacteria for the bioremediation of phenol derivatives in aqueous solutions. The principal application for the technology was in the wastewater treatment of chemicals that can be resistant to traditional treatments. The final student presentation was from Matthew Kirby of Imperial College London, who looked at the effect of siderophore desferrioxamine B on uranium precipitation. He specifically highlighted how the naturally occurring bacteria could cause uranium to precipitate out and affect groundwater quality surrounding nuclear facilities, including planned waste disposal facilities.

Our final speaker was Dr Laura Newsome from the University of Manchester. Laura talked about her career in chemistry and how she got her inspiration for science when visiting a museum with her parents. Following a first degree in Environmental Geology, she went to work in environmental consultancy, carrying out risk assessments and remediation of contaminated land. She subsequently spent some time at the Environment Agency looking at radioactivity before going on to do her PhD in the area of bioremediation of radionuclides in groundwater, which included field work in the USA. Her current work is on how microorganisms affect the fate and transport of cobalt in the environment.

To conclude the meeting, Laura presented the prize for the best oral presentation to Sarah Chandler from the University of Brighton.



## Meeting Report

# 6th International Symposium on Soil Organic Matter

Tom Sizmur (University of Reading)

More than 400 delegates from 44 different nations descended upon Rothamsted Research in Hertfordshire, UK, during four days in September 2017 for the 6th International Symposium on Soil Organic Matter, which saw more than 180 talks and 230 poster presentations

The conference opened with a welcome from Rothamsted Research Director Professor Achim Doberman, who introduced some of the long term experimental findings that make Rothamsted a world famous institute for the study of soil organic matter. Back when the Broadbalk experiment (now the longest continuously running agricultural experiment in the world) was started in 1843, the intention was to compare the standard practice of applying organic manure with the relatively new concept of mineral fertilisers. It is therefore ironic that there is renewed interest in the benefits associated with the elevated soil organic matter found in the manured plots compared to the benefits accrued from the modern mineral fertilisers.

Several themes emerged throughout the conference: perhaps the strongest of these was the need to develop the next generation of soil organic matter decomposition models and for experimental scientists to work more closely with modellers (and *vice versa*). This was first raised in a keynote address by Professor Michael Schmidt, whose 2011 paper in *Nature* (*1*) revolutionised the field by suggesting that 'stable' soil organic matter was not plant matter that had resisted decay over time due to its chemical composition, but in fact largely consists of microbial products that, despite being thermodynamically unstable, are physically and chemically protected from decomposition by soil aggregates and physical sorption on soil surfaces.

The challenge of generating the data to represent these processes in soil organic matter decomposition models was taken up by several presenters using stable isotopes to track the movement of carbon through soils, and was introduced in keynote presentations from Professors Francesca Cotrufo and Richard Evershed. Another experimental technique that dominated many talks was the use of physical fractionation methods. These methods use sieving and density separation to isolate fractions of the soil organic matter occluded within aggregates from fractions that are chemically adsorbed to soil surfaces. An interlaboratory comparison of several such protocols was presented by Dr Christopher Poeplau.

**“Listen to advice from experienced scientists. Consider the advice – sometimes act on it. But don’t be constrained by it – be bold and develop fresh ideas!”**  
- Professor David Powlson

Towards the end of the conference, Professor Henry Janzen gave an inspiring talk on the topic of soil health, providing a much-needed definition of soil health as being the combination of soil functions, vitality, and time. In agreement with most soil scientists, he identified soil organic matter as the preeminent indicator of soil health. Professor

Janzen asserted that a key facet of soil organic matter was as a dynamic repository of solar energy and that this solar energy, when respired by soil organisms, provides many of the ecosystem functions that are associated with healthy soils.

The conference ended with a closing ceremony in which Professor David Powlson gave a dedication to the late Professor David Jenkinson, who pioneered many of the techniques presented in the conference, including the creation of soil organic matter models, the measurement of the soil microbial biomass, and the use of stable and radioactive isotopes to study C and N cycling in soils. Powlson closed his talk with this advice to early career scientists: “Listen to advice from experienced scientists. Consider the advice – sometimes act on it. But don’t be constrained by it – be bold and develop fresh ideas!”

## References

1. Schmidt, M.W.I., et al., *Nature*, 2011. **478**(7367): p. 49-56.

## Meeting Report

# 27th V. M. Goldschmidt Conference, Paris, 14th – 18th August 2017

Laura Newsome (University of Manchester)

The Goldschmidt Conference is one of the largest geochemistry conferences in the world, with more than 4,200 abstracts accepted in 2017, generating 146 different sessions, run in parallel with up to 20 different talks to choose from at any one time ([goldschmidt.info/2017/](http://goldschmidt.info/2017/)). With such a varied programme, throughout the week I was able to attend presentations on subjects as diverse as weathering and climate, isotope geochemistry, microbial metabolism and seawater chemistry, the effects of mining deep sea nodules, and even gas generation in nuclear waste repositories.

One of my personal highlights of the conference was Wednesday's plenary lecture by H el ene Langevin-Joliot of CNRS (the French National Centre for Scientific Research), talking about her life as a scientist, but also about the life and work of her rather famous grandparents, Pierre and Marie Curie. It was very interesting to hear about their personal lives, as well as their pioneering achievements in the discovery of radium and polonium.

I chaired a session on the Friday entitled "The Mineralogy and Geochemistry of Metal Deposits and Secondary Sources". We selected a range of abstracts for oral and poster presentation to encompass a range of topics relevant to the chemistry of metal deposit formation and metal recovery. The session started with talks on the geochemistry of metal deposits, covering how rare earth elements and precious metals had become enriched in ore bodies. Then the focus of the session switched to laterites, highly weathered rocks



**Figure 1.** H el ene Langevin-Joliot talking to a packed auditorium about her famous grandparents Pierre and Marie Curie (photograph taken by Laura Newsome).

that are currently our largest source of nickel, but are increasingly being considered as a resource for cobalt and scandium. ([www.nhm.ac.uk/our-science/our-work/sustainability/cog3-cobalt-project.html](http://www.nhm.ac.uk/our-science/our-work/sustainability/cog3-cobalt-project.html)).

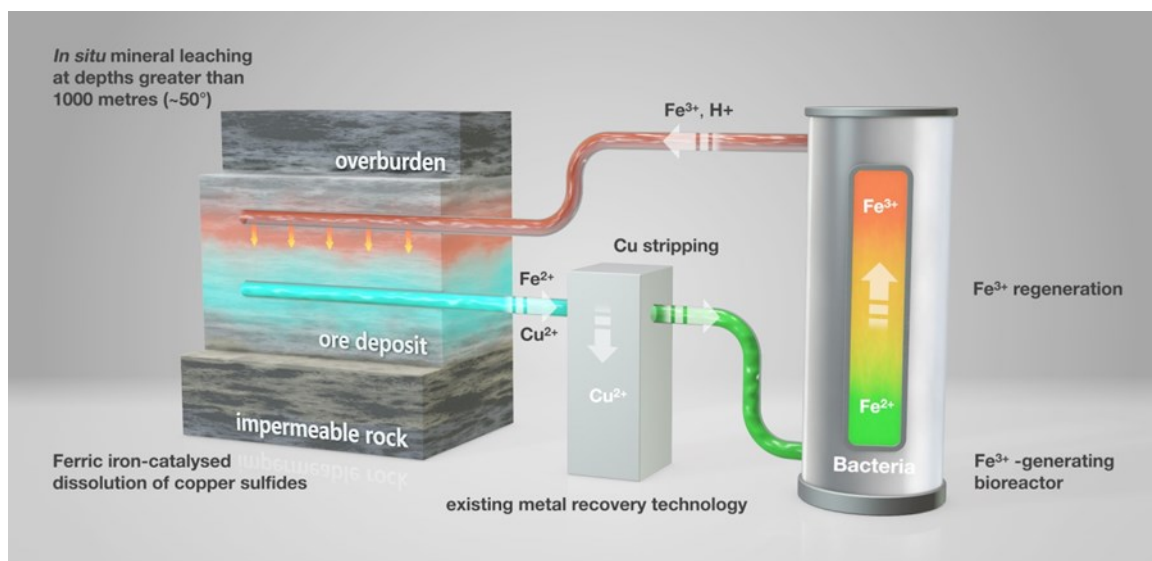
The keynote talk was given by Professor Frances Wall on processing ores to recover rare earth elements (REE). There are concerns about the security of supply of REE, increasingly used in modern technologies such as wind turbines and electric cars, and therefore the European Commission has highlighted REE as critical raw materials ([www.bgs.ac.uk/sosRare/home.html](http://www.bgs.ac.uk/sosRare/home.html)). It was interesting to hear about the different types of deposits containing REE. For example, mineral sands which are rich in REE and are the easiest deposit to process; however, they also contain high concentrations of uranium and thorium which means that it is unlikely that they will be exploited commercially. Absolutely crucial in the process of REE recovery is the chemistry of froth flotation which uses surfactants and frothing agents to selectively separate minerals with different hydrophobicities. This allows the REE-containing minerals to be separated from the rest of the material, and further processing is then required to separate the different REE from each other.

Subsequently the talks switched to research on new techniques of metal recovery, such as retrieving metals from secondary sources (e.g. mine tailings and incineration residues). These new methods are designed to be more environmentally friendly than traditional mining. One area that generated lots of discussion was the BIOMore project ([www.biomore.info](http://www.biomore.info)). This project

aims to develop innovative and environmentally sustainable technologies to recover metals from deep mineralised horizons *in situ*, therefore making new commodities available that are inaccessible using traditional mining techniques. The research presented involved laboratory-scale studies and modelling of bioleaching of copper sulfide minerals in the Polish Kupferschiefer sandstone deposit (**Figure 2**), but this is yet to be tested in the field. This technology uses iron(II)-oxidising acidophilic bacteria to produce ferric iron, which would then be pumped into the mine *via* horizontal fractures. The ferric iron then oxidises the sulfide minerals under acidic conditions, releasing iron(II) and copper to the aqueous phase. This leach solution is then pumped to the surface where the copper can be recovered, and the iron(II) returned to the bioreactor for recirculation. The results presented showed that the Kupferschiefer sandstone contains carbonate minerals which will require prior removal by acid leaching as they have a significant pH buffering capacity and therefore would have an adverse impact on the bioleaching process.

The most pleasing feature of the session was an introduction to the more 'exotic' side of the periodic table, with many elements discussed that I had not known much about before, such as tellurium, lithium, tantalum, gallium, all of which are becoming more and more essential in the modern economy.

For more information about the Goldschmidt conferences including future conference dates visit <https://goldschmidt.info/>.



**Figure 2.** Schematic representation of *in situ* indirect bioleaching of a deep-buried copper sulfide ore ([www.biomore.info](http://www.biomore.info)). © DMT GmbH & Co. KG/Germany

## Article

# Emerging organic contaminants

Jamie Harrower (PhD Researcher, Glasgow Caledonian University/  
James Hutton Institute)

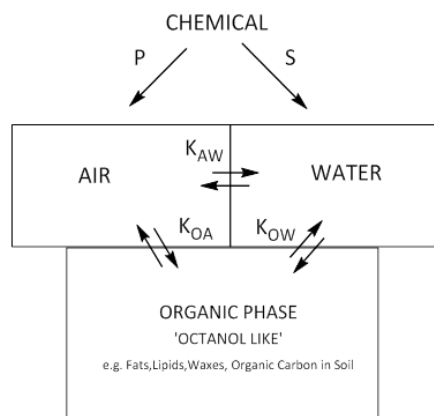
Emerging organic contaminants (EOCs) have attracted the interest of the international science community, with numerous studies demonstrating the presence of EOCs in significant concentrations within the environment. The term emerging organic contaminants relates to newly synthesised compounds that are recognised as hazardous to wildlife, ecosystems, and potentially humans. Advances in analytical technologies have created instruments capable of detecting such compounds at low concentrations, even within complex matrices.

Until the early 1990s, non-polar persistent organic pollutants (POPs) and heavy metals were the main focus of intensive monitoring programmes; these include poly-aromatic hydrocarbons (PAHs) such as fluoranthene and benzo[*a*]pyrene and hydrocarbon solvents such as toluene and xylene (1). Today, these compounds are less relevant in industrialised countries thanks to drastic emission reductions. However, because of their extensive historical use and presence within industry, significant levels persist within the environment.

## Fate of EOCs

Emerging organic contaminants are generally hydrophobic by nature, with varying degrees of polarity, and varying physicochemical properties ( $pK_a$ , water solubility, partition coefficient and vapour pressure). Triclosan, Carbamazepine and Diclofenac are typical EOCs (with vapour pressure values of  $6.9 \times 10^{-5}$  Pa,  $1.17 \times 10^{-5}$  and  $2.91 \times 10^{-4}$  Pa, respectively) and can be present in different physical states under particular environmental conditions. The fate and transport of EOCs within the environment is heavily dependent on their physicochemical properties and the surrounding environmental conditions, such as pH of the aqueous phase and soil composition. EOCs can

**The main contributor of emerging organic contaminants to the environment is the discharge of treated wastewater**



**Figure 1.** Physico-chemical properties that control the environmental partitioning of organic chemicals within the environment. *P* = vapour pressure, *S* = solubility, *K* = partition coefficient.

also degrade or transform into metabolites, which in turn are able to partition and migrate into other phases in the environment, making it challenging to predict their behaviour. The transfer of chemicals between two or more environmental compartments can be described by equilibrium partitioning, which takes place between adjacent phases such as between a solid and a liquid (dissolution) or a liquid and a gas (volatilisation) (2). This net transfer of an organic compound between phases is limited by equilibrium constraints and can be quantified according to partition coefficients (Figure 1).

Several partition coefficients are essential for understanding chemical transfer in the environment as well as the fundamental properties of vapour pressure (*P*) and solubility of a compound (*S*). Important partition coefficients that determine a chemical's fate include air/water ( $K_{aw}$ ), n-octanol/water ( $K_{ow}$ ) and n-octanol/air ( $K_{oa}$ ). The aqueous solubility and vapour pressure (effectively the solubility of a chemical in air) of a compound determine the partitioning of a chemical from pure liquid or solid into air and water.

## Sources and classes of EOCs

EOCs are found in pharmaceutical and personal care



products, pesticides, veterinary products, industrial compounds/by-products, food additives, and engineered nano-materials. The rise in EOCs in recent years has resulted in a swift response from the science community.

Organic contaminants can enter the environment through landfill sites, animal and domestic waste, hospital and industrial effluent, septic tanks and waste water treatment plants (WWTPs). In developed countries, the main contributor of EOCs to the environment is the discharge of treated wastewater from WWTPs (3). Studies have been conducted throughout Europe showing the presence of 125 different polar organic compounds within the effluent of 90 WWTPs (4).

The impact of these contaminants on human health is often unknown, however some organic compounds have been classed as Endocrine Disrupting Compounds (EDCs) and have been detected in sewage sludge and sewage sludge-amended soils. EDCs can also cause adverse effects on wildlife and the ecological system (5). A well-known EDC is Bisphenol A (Figure 2), which has recently been placed on the list as a substance of very high concern (European Chemicals Agency).

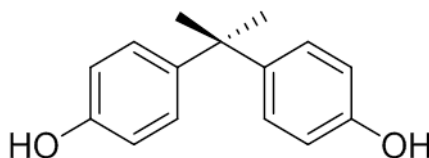


Figure 2. Bisphenol A

## Wastewater treatment processes

Technology at WWTPs is continually improving and developing to ensure the safe and effective treatment of raw sewage. The activated sludge process is the most extensively implemented secondary wastewater treatment process and is effective at removing carbonaceous material and certain nutrients (6). Many drugs of anthropogenic origin are removed through biological degradation and sorption onto solids. However, their varying degrees of sorption and biodegradation make enhanced EOC removal rates at WWTPs very different. Also, many pharmaceutical and organic compounds have low vapour pressures, which restricts them from being removed by volatilisation. It should be noted that for several processes, removing the pollutant from the water simply transfers it to solid waste or the atmosphere.

To further enhance EOC removal following the secondary waste effluent treatment process, tertiary processes have been tested, such as biofiltration (sand or trickling filters), chemical oxidation and adsorption by activated carbon (6). However, once again, the efficiency of the removal processes is highly compound-specific.

## Sample preparation and analytical procedures

Analytical techniques such as Gas Chromatography- Mass

Spectrometry and Liquid Chromatography-Mass Spectrometry are the most commonly applied techniques for detecting compounds within environmental matrices. Many studies have used the triple quadrupole mass detector (MS/MS), which offers the ability for enhanced mass fragment analysis of micropollutants. Sample pre-treatment is crucial when analysing trace contaminants at concentrations in the  $\text{mg L}^{-1}$  or  $\mu\text{g L}^{-1}$  scale in environmental samples, but is particularly important for extracting solid (soil) mixtures. Accelerated solvent extraction (ASE) provides a selective and efficient extraction by drawing solvent mixtures through a metal sample cell at high pressure (7). Further sample clean up using solid phase extraction (SPE) may be required after extraction is complete, and depending on what analytical technique is employed for analysis, a sample derivatisation step may also be needed.

The release of EOCs to the environment will continue as new consumer products are constantly being brought to market. Therefore, the challenge to remove and prevent EOCs from entering the environment remains an international task. Legislation to control and minimise the release of dangerous chemicals into the environment, such as the Water Framework Directive (WFD, Directive 2000/60/EC) aim to meet certain environmental quality standards in all surface and ground waters (rivers, lakes, transitional waters and coasts), with a focus on protecting ecology and wildlife. The directive 2013/39/EU, amending the Environmental Quality Standards Directive 2008/105/EC under the European WFD, has introduced a new "Watch list" monitoring mechanism to collect high-quality EU-wide monitoring data of potentially polluting substances in the aquatic environment. To date, there are numerous other pharmaceutical compounds detected within the environment, which are continually being considered for the "Watch list".

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## Article

# Chlorine-based water disinfection

Glynn Skerratt

In the mid-nineteenth century, Britain suffered a succession of cholera epidemics. In 1848, there were 14,000 deaths attributable to the disease in London alone, reflecting the lack of appropriate sanitation. Famous Victorian pioneers such as Edwin Chadwick and Dr John Snow first linked the transmission of cholera to polluted drinking water. Snow demonstrated that the cholera was caused by contaminated water rather than the atmospheric 'miasma' that had previously been thought to be responsible. The memorably named Thomas Crapper carried out much of the early domestic sanitation work in the UK capital and, together with Sir Joseph Bazalgette, revolutionised the sewerage system.

Even now in the 21st century, there are still tens of thousands of deaths worldwide every day that are directly attributable to the lack of clean water. Water can be biologically contaminated with bacteria, viruses, protozoa and nematodes. Disinfecting the water enables us to destroy these disease-causing agents or pathogens, rendering the water drinkable or 'potable'.

## Microbiology

Most outbreaks of waterborne disease are caused by contamination of water supplies with animal or human excreta. Microbiological testing is carried out to check whether water is fit for consumption by testing for the presence or concentration of a number of *indicator organisms* that are:

- abundant and found exclusively in faeces but (almost) absent elsewhere

- no less resistant to disinfection than other pathogens (and preferably a little more so)
- persistent in the environment
- unable to grow or multiply in the aquatic environment
- cheaply, rapidly and reliably detectable

*Escherichia coli* is readily distinguishable and is associated with the gut of humans, mammals and fish. Whilst water containing coliform bacteria other than *E.coli* can be assumed to have some bacteriological contamination, water that contains *E.coli* is assumed to be contaminated with animal excrement. The UK Water Supply (Water Quality) Regulations detail Prescribed Concentrations and Values (PCVs), which stipulate that both *E.coli* and coliform bacteria should not be detectable in any 100 mL sample volume of water.

**Even now, in the 21<sup>st</sup> century, there are still tens of thousands of deaths worldwide each day that are directly attributable to the lack of wholesome water**

In 1908, a British microbiologist, Dr Harriette Chick, described the reduction in microorganisms following disinfection as a first-order reaction where the rate of reduction in microorganisms with time can be expressed as:

$$dN/dt = -kN$$

where:

$N$  = number of microorganism ( $N_0$  is the initial number)

$k$  = a (disinfection) constant

$t$  = contact time

The integral of this expression is known as Chick's Law and forms the basis for determining the effectiveness of a disinfection process (often simplified to depend solely on disinfectant concentration 'c', and the contact time 't' of the disinfectant with a pathogen):

$$N = N_0 e^{-kt}$$

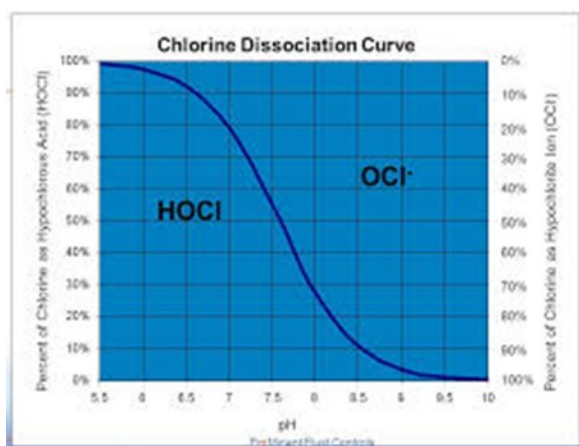
## Disinfecting Water

A disinfectant needs to reduce pathogen concentrations within a reasonable amount of time and at a reasonable temperature. There are a number of controllable process variables, including the nature, concentration and

distribution of the organisms to be destroyed, the contact time of the disinfectant with the water, the condition of the water to be treated (amount of suspended/organic matter, pH, temperature, etc.) and the presence of other compounds capable of reacting with the disinfectant. Historically throughout the UK a technique known as 'breakpoint chlorination' has been used to underpin our mains water microbiological quality.

## Chlorine-based disinfection

Use of the chlorine-based disinfectant hypochlorous acid (HOCl), formed when chlorine gas mixes with water, is probably the most widely used means of drinking water disinfection in the UK. The following equilibrium is established:

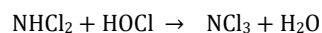
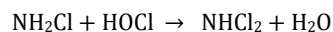
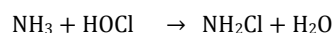


**Figure 1.** pH dependency of hypochlorous acid-hypochlorite ion equilibrium [source: <http://slideplayer.com/slide/6973575/> (slide 16)]

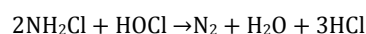
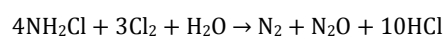
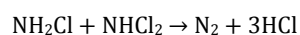
Bulk chlorine gas tends to be used as the feedstock at larger water treatment sites, while pre-mixed solutions of hypochlorite salt can be used at smaller treatment works. On-site electrolytic chlorination (OSEC) is also used on some smaller sites where a concentrated solution of sodium chloride is electrolysed to form chlorine directly.

In solution, most HOCl remains undissociated below pH 7 but above pH 8, most becomes dissociated. This equilibrium is important because electronically neutral HOCl is a strong disinfectant, whereas the charged  $\text{ClO}^-$  ion is 80-100 times less effective. The sum of the concentrations of HOCl and  $\text{ClO}^-$  ions is known as the free available chlorine (FAC).

Ammonia can be present in natural waters and HOCl reacts with it in a stepwise manner, producing chloramines, which are weaker disinfectants.



When the molar ratios of  $\text{ClO}^-$  and  $\text{NH}_3$  are similar, monochloramine ( $\text{NH}_2\text{Cl}$ ) tends to be the predominant reaction product. The total amount of dichloramine ( $\text{NHCl}_2$ ) and monochloramine is called the combined available chlorine (CAC). When excess chlorine is present, more chloramines form. Eventually, all of the ammonia is removed from solution and the monochloramine and dichloramine then react together, resulting in products which are not disinfectants:

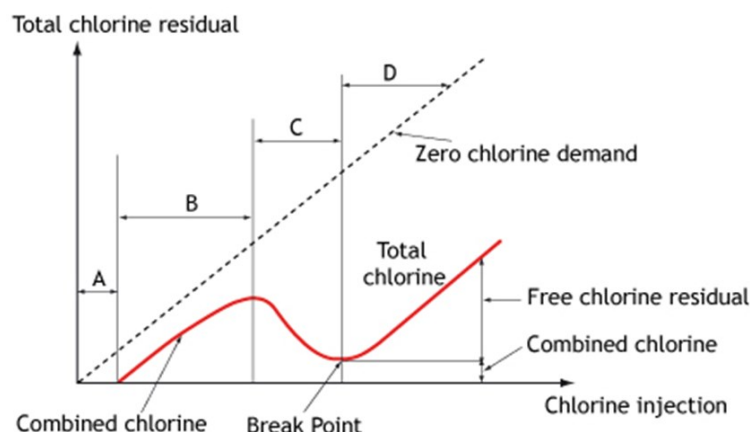


The 'breakpoint' occurs when the chlorine residual drops back to almost zero and all of the ammonia that was originally present has been oxidised to nitrogen. Further addition of chlorine beyond the breakpoint ensures the presence of free available chlorine and an appropriate disinfecting environment.

Increasing the ratio of chlorine to ammonia beyond 5:1 results in some of the monochloramine reacting to form small amounts of dichloramine. As the ratio approaches 7.6:1 (Figure 2, C), the chloramine is oxidised by the excess chlorine to nitrogen gas, resulting in a rapid loss of residual chlorine from the water. The point between C and D (Figure 2) is the breakpoint. After this point, there is no ammonia left to react with the chlorine and the residual chlorine concentration then increases in proportion to the amount of chlorine added.

Total residual chlorine (TRC), or total chlorine, is a measure of the combined available chlorine and the free available chlorine after demand has been met. It is possible that while the TRC value remains constant, the relative concentrations of the different chlorine compounds can vary widely, depending on factors such as pH and the relative concentrations of any species that can combine with chlorine.

At the waterworks, freshly chlorinated water flows into a contact tank to ensure complete mixing. The effective contact period in this tank is usually defined in terms of the  $t_{10}$  residence time – the time for which 90% of the incoming flow has a longer residence. The target concentration for free chlorine in the water for



**Figure 2.** Breakpoint chlorination curve [source : <https://endotlmsnewsdotorg.wordpress.com/2011/11/17/chlorine-disinfection/>]

distribution into supply is typically in the range 0.2-2.0 mg L<sup>-1</sup> although sometimes it can be up to 5.0 mg L<sup>-1</sup>.

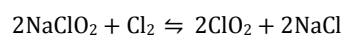
Sometimes a process called superchlorination is employed, involving the addition of large amounts of chlorine to destroy odours and tastes or to ensure a 'quick kill' of pathogens. If the water treated this way were then simply distributed, with its relatively high HOCl and ClO<sup>-</sup> concentrations, it would be disinfected but unpalatable. Therefore water is partially dechlorinated after superchlorination, by adding a reducing agent designed to leave a residual chlorine concentration of about 0.5mg L<sup>-1</sup>. Usually sulphur dioxide gas (SO<sub>2</sub>) is used, although alternatives include sodium bisulfite (NaHSO<sub>3</sub>) or sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>).

One of the disadvantages of using chlorine is that it can react with any natural organic matter (NOM) in the treated water to form disinfection byproducts (DBPs). The most common of these is a group of compounds called trihalomethanes (THMs). Trihalomethanes are a group of halogen-substituted organic compounds, and have the general formula CHX<sub>3</sub> where X can be any halogen or combination of halogens and commonly include chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl) and bromoform (CHBr<sub>3</sub>). These THMs are all considered to be possible carcinogens, and current water quality regulations stipulate a PCV of no greater than 100 µg L<sup>-1</sup> (total) at the tap.

Chloramination is an alternative disinfection process that involves the addition of anhydrous ammonia gas (NH<sub>3</sub>) or ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) to chlorinated water to achieve an ammonia:chlorine ratio of 1:3, and thereby intentionally generate chloramines as the disinfecting species. In the UK, this process has historically been used

to disinfect much of the mains water in the London area. Chloramination offers a mechanism for long-term disinfection without creating taste problems. However, chloramination is a less powerful disinfectant than HOCl and it therefore requires a longer contact time.

Chlorine dioxide (ClO<sub>2</sub>) can also be used as a disinfectant and, although not common in the UK, is used extensively in the US. It is a gas at normal temperature and pressure and is prepared on-site from the reaction of sodium chlorite (Chloritane) with chlorine, or hydrochloric acid.



Normally an excess of chlorine is used to drive the reaction to the right.

Chlorine dioxide does not react with ammonia, nor create any taste problems, even at relatively high concentrations. It also has the advantage of long-lasting residual disinfection, making it particularly suitable for long distribution mains.

### Further resources

The Wellcome Trust has information on its website about the history of water treatment and diseases. (<https://blog.wellcome.ac.uk/2009/06/09/a-history-of-legionnaires-disease-in-the-uk/>)



## Article

# Antibiotic resistance – Antibiotic release into the environment

Roger Reeve (University of Sunderland)

Antibiotics are drugs used to treat bacterial infections in humans, animals and fish. Every few weeks, major news items about the crisis of antibiotic resistance for medicinal use surface, often stating that, in the near future, there will be few antibiotics available for the treatment of infections due to overprescription. Deaths are predicted from everyday infections and safe medical procedures (1, 2). Public concern persists around the issue, and is often heightened after the publication of major national or international surveys (3-7).

The first antibiotic, penicillin, was discovered in 1928 and began to be used in 1942. Resistance was first observed in 1936. It is common for resistance to be

detected within a few years of the introduction of a new antibiotic (8). No new classes of antibiotics have been brought into the market since 1987 (6).

Reports indicate resistance control must be multi-faceted, minimising levels in the wider environment (where resistance may build up) as well as controlling medicinal use in hospitals and by prescription. In some countries, antibiotic use in farming and veterinary science can exceed its use in humans, often with less strict control. Resistance built up through agricultural use may also ultimately affect human medicinal use. Legislation can be different for human and animal use and may lead to the situation where a drug strictly regulated for the former use is used more freely for the latter.

## Build-up of Environmental Resistance

Build-up of environmental resistance depends on both chemistry and microbiology. It is first established in a bacterium in a defined geographical location. However, bacteria multiply quickly, doubling their numbers every 20-30 min. Transfer of resistance may then occur

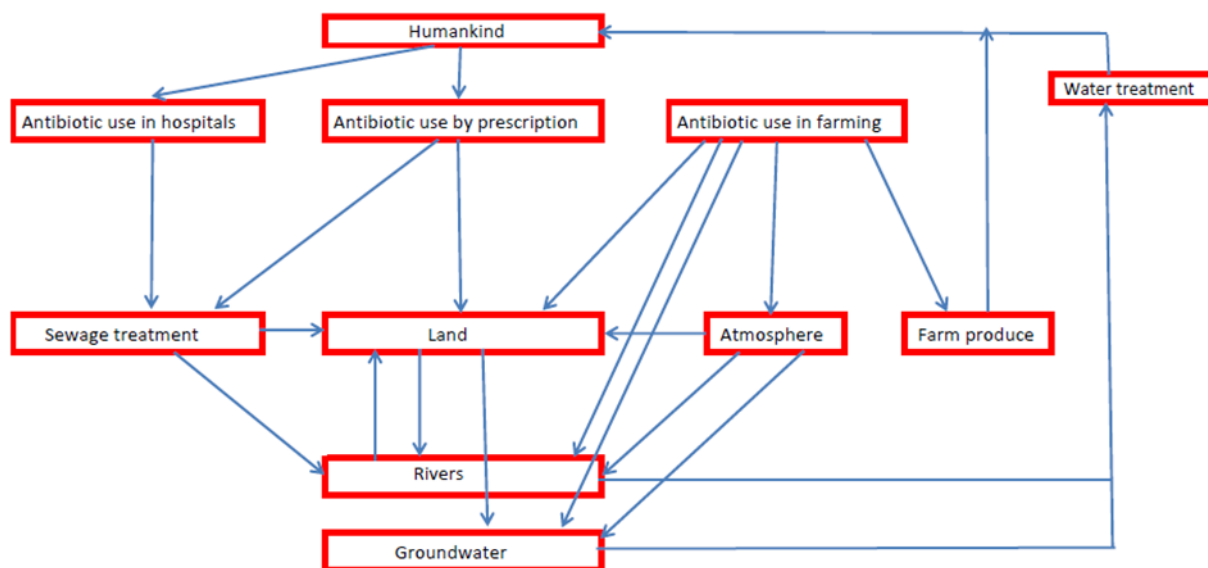


Figure 1. Environmental cycle of antibiotics in developed countries.

between the bacteria through the development of antibody resistance genes (ARGs), and selection pressure may favour their replication. Discussion of the role of the environment in the build up of antibiotic resistance thus runs on two parallel tracks: the build-up of resistance and the transmission of ARGs back to humans. Whether, or how, the resistance is transferred to organisms affecting human health is the subject of intense scientific debate.

## Antibiotic Types and Behaviours

Chemical antibiotics can be divided into groups (9,10), as shown in Table 1.

**Table 1.** Antibiotic groups with typical examples

Group	Typical example
Penicillins	penicillin, amoxicillin
Cephalosporins	cephalexin
Macrolides	erythromycin, clarithromycin, azithromycin
Fluoroquinolones	ciprofloxacin, levofloxacin, ofloxacin
Sulfonamides	sulfamethoxazole
Tetracyclines	tetracycline, doxycycline
Aminoglycosides	gentamicin, tobramycin
Polymixins	colistin

Antibiotics used in humans can be broad spectrum antibiotics (e.g. amoxicillin, tetracycline, aminoglycosides, and second and third generation cephalosporins), or narrow spectrum antibiotics which cause less resistance (macrolides, and older penicillins). Broad spectrum antibiotics are useful if the source of the infection is unknown. Some antibiotics, such as the fluoroquinolones and colistin, can have severe side effects and are only used in the last resort (10, 11).

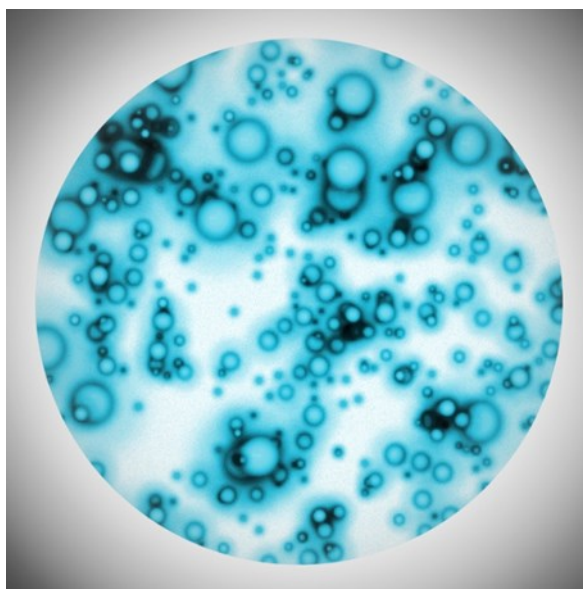
In 2013, the NHS England (National Health Service) reported that around one in five *E. coli* infections were resistant to a commonly used antibiotic (ciprofloxacin), an 18% increase since 2010. Resistance build-up is geospecific – ciprofloxacin resistance ranges from 25% in London to 12% in Cumbria, Northumberland, and Tyne and Wear (12).

## Release Mechanisms

In developed countries, antibiotics primarily enter the environment through sewage treatment plants (Figure 1). Antibiotics administered medicinally pass through the body and are discharged partly as the unchanged antibiotic, partly as metabolites, and partly as glycoside or sulphate conjugates. For example, ~20% of sulfamethoxazole (a sulfonamide antibiotic) is excreted in urine unchanged, 15–20% as a glucoside conjugate, and 50–70% as the acetylated derivative (13). Some

metabolites may retain the pharmaceutical activity of the original drug. Conjugates can break down during treatment and the wider environment, reforming the original antibiotic. Unused antibiotics prescribed for home use may also be disposed of in household waste.

Most waste treatment plants have primary and secondary treatment processes with tertiary treatments reserved for specific contaminants which are problematic at given locations. The primary treatment is sedimentation to remove solids. Secondary treatment uses aerobic conditions to degrade organic material using populations of microorganisms. Resistance may build up in bacteria (14) during sewage digestion. Antibiotics in the sewage sludge can be returned to the environment if this digested sewage is used untreated as a soil conditioner or disposed of in landfill. The main tertiary treatment methods include ozonolysis, chlorination and UV treatment. These disinfect the water and remove specific components by chemical degradation. Removing antibiotics during sewage treatment depends not only on the treatment processes but also on the plant operational parameters such as the residence time of the wastewater (15, 16). In a study of four treatment plants (15), none of the antibiotics studied were eliminated completely, with the maximum efficiency reaching 81%. Macrolides, especially erythromycin, were stable throughout the treatment process.



**Figure 2.** Virus, Bacteria, Cell, Algae, Microbes.  
Credit: GiroScience/Shutterstock

Freshwater systems can contain a large number of pharmaceutically active compounds including antibiotics (17). Subsequent transport of antibiotics through the environment can be predicted from their chemical properties. Erythromycin ( $pK_a$  8.9, estimated  $K_{o/c}$  570, estimated vapour pressure 21–25 mmHg at 25°C), exists almost entirely in the cationic form in water so little volatilisation would be expected. It is expected to adsorb to suspended solids and sediment, have low mobility in soil and to exist in the atmosphere solely in the particulate phase (21).

Environmental mobility depends upon a substance's chemical properties. Sulfamethoxazole ( $pK_a$ s 1.6, 5.7, estimated  $K_{o/c}$  72, estimated vapour pressure  $6.9 \times 10^{-8}$  mmHg at 25°C) is not expected to adsorb onto suspended solids and has low volatility in water. In general, sulfonamide

antimicrobials are not readily biodegradable. They persist in soils and are highly mobile. In the atmosphere they probably exist in both vapour and particulate phases and the potential for bioconcentration in aquatic organisms is therefore estimated to be low.

Farm animals are often given antibiotics both prophylactically and therapeutically in their water or feed. Prophylactic use is often equated to bad farming practice. Antibiotics have also been used at sub-therapeutic levels as growth hormones, but this has been banned in the EU since 2006, and, in January 2017, new rules were introduced in the US (18, 19).

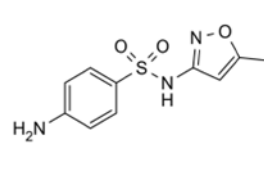
Antibiotics and their metabolites can enter the environmental cycle via animal excretion, manure use (e.g. field spraying), and transfer to rivers through run-off. Farm produce is directly handled and consumed by humans. In less developed countries, where water is either not treated or poorly treated, direct consumption of water may also be a significant route.

## Policy

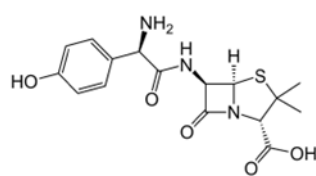
Over the past three years, many major international organisations have produced extensive reports on

antibiotic resistance, including campaigns to increase public awareness and improvement in sanitation, reducing the unnecessary use of antimicrobials in agriculture and their dissemination in the environment, and improving global surveillance of drug resistance and antimicrobials consumption in humans and animals.

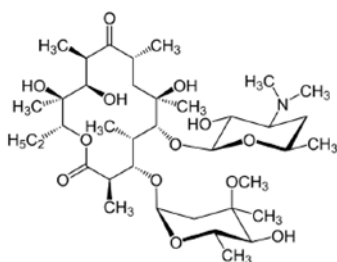
The UK Government announced a reduction in the number of inappropriate prescriptions, working internationally to develop and make available new antibiotics, and an overall target for antibiotic use in livestock and fish farmed for food - cutting use by 2018 to the level recommended in the O'Neill report (5,6).



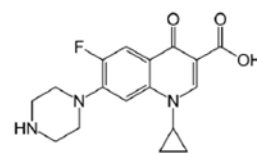
(b) Sulfamethoxazole



(a) Amoxicillin



(c) Erythromycin



(d) Ciprofloxacin

**Figure 3.** Structures of typical antibiotics

The US National Action Plan for combating antibiotic-resistant bacteria (4) aims to slow the emergence of resistant bacteria in both public health programmes and farming, including supervision of veterinary and agricultural uses.

The EU Action Plan against Antimicrobial Resistance (7) stresses the need for international cooperation and the development of new therapeutics, vaccines, and technologies.

Current EU legislation identifies the macrolide antibiotics erythromycin, clarithromycin and azithromycin as posing significant threat to environmental life, and placed them on the watch list of substances (20) as defined by Directive 2008/105/EC (22). These had previously been listed by the WHO in 2011 as critically important for human health (23). Recommendations from the European Medicines Agency (EMA) for use of a human last resort antibiotic, colistin, suggest limiting its application in farming, rather than banning it completely, and improving animal husbandry rather than replacing antibiotics (24).

The rapid publication of national and international reports is an indication that governments are realising the necessity to prevent the spread of antibiotic resistance and that control within the environment is an important tool in the overall strategy.

To learn more about this topic, register for “**Biopollution: Antimicrobial Resistance in the Environment**” The Distinguished Guest Lecture of the Royal Society of Chemistry Environmental Chemistry Group will be held on 28th March 2018 12:00-17:00, London, United Kingdom (*see pp. 21-22*).

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## Upcoming Meeting

# Biopollution: Antimicrobial Resistance in the Environment

Where: The Royal Society of Chemistry, Burlington House, London, W1J 0BA

When: Wednesday 28th March 2018 12:15 pm

This one-day symposium organised by the Environmental Chemistry Group of the Royal Society of Chemistry explores the chemistry and biochemistry of antimicrobial resistance in the environment, the policy relating to it and its effects on human health. The 2018 ECG Distinguished Guest Lecture will be provided by Professor Joakim Larsson (University of Gothenburg).

**Dr Andrew Singer (Natural Environment Research Council, Centre for Ecology & Hydrology)**



*Dr Andrew Singer*

Andrew Singer is a molecular microbial ecologist with expertise in pollution chemistry and water quality assessment and mitigation. He is Co-I and PI on two recently funded projects: 1) catchment scale molecular analysis and aetiology of antibiotic resistance genes (NERC), 2) the role of antibiotics and antimicrobial resistance gene dissemination from wastewater on AMR selection and maintenance in river systems (Cross-Research Council). He works with members of UK public health, and, through a collaboration with the Environment Agency, Defra and the Veterinary Medicines Directorate, helped to identify knowledge gaps in 'AMR in the Environment'. He has served on the UK Scientific Pandemic Influenza Advisory Committee, and Steering Committee for a US Department of State led workshop on "Mapping the Lifecycle of Antibiotics in

Southeast Asia" in collaboration with the US Geological Survey and Society of Environmental Toxicology & Chemistry.

*"An Environmental Chemist's Introduction to the Global Crisis of Antimicrobial Resistance?"*

Among the factors contributing to antimicrobial resistance (AMR) in the environment is the release of sewage and manure. The chemical composition of human and animal waste, such as antibiotics, antifungals, metals and biocides, are considered the major causative factors for maintaining the selective pressure on microorganisms during waste treatment and wider dissemination into the environment. The bacteria within the waste also contain AMR and represent a 'biological pollution', contributing to the spread of existing and novel environmental AMR. Research will be presented aimed at supporting the alleviation of the environmental burden of AMR and the risk it poses to human health, and a discussion of knowledge gaps and the need for policy-informing research.

**Professor Celia Manaia (Universidade Católica Portuguesa)**



*Professor Celia Manaia*

Celia M. Manaia works at the School of Biotechnology of the Portuguese Catholic University, where she is a member of the Environmental Research Group Diagnosis of the Centro de Biotecnologia e Química Fina (CBQF). She is Vice-President for Research and Internationalization of the Porto Regional Center of the Portuguese Catholic University. Her research is focussed on bacterial ecology in human-impacted environments, with emphasis on the spread of antibiotic resistance over the urban water cycle

and water-soil interface. She uses culture-dependent and culture-independent methods to study the dynamics of bacterial communities. She collaborates on various international projects, including STARE, NEREUS, ANSWERS, NORMAN-WG5, and HEARD.

*"Antibiotic Resistance – from Nature to Environmental Contaminants."*

This talk will focus on how the use of antibiotics and other factors may have forced antibiotic resistance genes to become a public health threat. Professor Manaia will explore municipal wastewater treatment plants as potential sources of contaminant antibiotic resistance and some measures that may help avoid antibiotic resistance dissemination. She will finish by discussing how to assess the risks these environmental contaminants represent for human health.

### **Mr Lee Slater (Department for Environment, Food and Rural Affairs)**



*Mr Lee Slater*

Lee Slater is Senior Policy Advisor in the Water Quality Team in Defra, and is responsible for the Antimicrobial Resistance in the Environment group. He has an MSc (Distinction) in Environmental Science, Legislation and Management, and a 16 year career in commercial and marketing strategy.

*"Anthropogenic Sourced Antimicrobial Resistance in the Environment – Implications to Policy and Environmental Management Practice."*

The natural environment is immensely complex and varied. This multiplies the challenges to regulators and stakeholders in addressing the hazard of AMR. In recent years academic research has improved our understanding of the anthropogenic routes to and confluences within the environment. Furthermore it is evident that a robust AMR program will also need to address the management of biocides and heavy metals; both are known to influence AMR responses in bacteria. Lee Slater will speak on the policy implications of current and pending academic research, and the opportunity for environmental chemists to contribute to the issues.

### **Distinguished Guest Lecture: Professor Joakim Larsson (University of Gothenburg)**



*Professor Joakim Larsson*

Joakim Larsson is a Professor in Environmental Pharmacology. He holds a PhD in animal physiology, and a background in marine research. In 2007, he combined his interests in the environment and medicine, entering the field of human physiology, and becoming professor at the University of Gothenburg in 2013. He is now the director for the Centre for Antibiotic Resistance Research, involving more than 100 researchers from six faculties. His papers include the identification of ethinylestradiol as an important contributor to the feminization of wild fish, and studies showing manufacturing discharges cause the most severe cases of environmental pharmaceutical pollution. Current research includes work on the role of antibiotics, metals and antibacterial biocides in the promotion of antibiotic resistance, exploration of the environmental resistome for novel resistance genes, evaluation of advanced effluent treatment technologies, surveillance of resistance in the human population using sewage bacteria, and aquatic and aerial transmission of AMR pathogens.

*"Selection of Antimicrobial Resistance in the Environment."*

### **Registration**

**EARLY BIRD:** £50/£35/£22.50 (standard/ECG member/student) 28th February 2018

**STANDARD:** £65/£50/£22.50 (standard/ECG member/student) 19th March

*There are a limited number of free places available for unemployed and retired members. To apply, email Dr Rowena Fletcher-Wood, [ecg.dgl@gmail.com](mailto:ecg.dgl@gmail.com). All registrations are non-refundable, but delegate passes may be exchanged.*

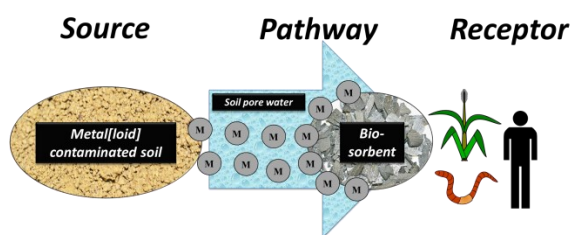
# The application of modified bio-sorbents to heavy metal[loid] contaminated soils

Luke Beesley (The James Hutton Institute) Eduardo Moreno-Jimenez (Universidad Autónoma Madrid)

Lukas Trakal (University of Life Sciences Prague)

Combining bio-sorbent materials together in a single soil amendment offers a way to simultaneously reduce the environmental mobility of co-occurring, geochemically dissimilar heavy metal[loid]s.

The risk assessment of contaminants in the environment can be summarised using a source-pathway-receptor model (1). In the context of heavy metal[loid]s and their potential to cause environmental harm, remediation methods should seek to break the pathway between the source and receptor (Figure 1). The complex geochemistry of soils means that a high concentration of metal[loid]s may not always be analogous to an increase in the risk to receptors. This is because metal[loid]s can be more or less strongly bound to different constituents of the soil matrix under different environmental conditions. By focusing remediation on metal[loid]s that are weakly bound to the soil matrix, their mobility in the environment can be substantially reduced, and thus risk minimised (2). It is possible to modify soils by adding bio-sorbents *in situ* to ensure stability of the most weakly bound contaminants, reducing potential risk and avoiding the need for the removal and *ex situ* soil treatments.



**Figure 1:** Diagrammatic representation of the role of bio-sorbents in addressing environmental risk posed by elevated metal[loid]s in soil pore water.. Adapted from (3)

## Mechanisms of heavy metal influence by bio-sorbants

A wide range of soil amendment materials that act as bio-sorbents have been extensively tested in both laboratory and field trials, including using composts, manures, sludges, digestates, activated and non-activated chars, etc. They may be used at various stages from source material to final product, and exhibit a wide range of physico-chemical compositions.

In general, oxygen containing functional groups at the surfaces of organic bio-sorbents result in a cation-exchange-capacity (CEC) greater than that of the soil they are added to. They act as a sink for metal ions in solution, limiting their leaching and/or uptake in plants. However, bio-sorbents contain compositional artefacts which limit their effectiveness in soils: organic materials often exhibit high concentrations of dissolved-organic-carbon (DOC) leaching; complexes of metals with organic ligands can result in the co-leaching of DOC-associated metals in solution; and many char-based sorbents have high residual ash content, which results in temporary precipitation of metal ions with mineral salts within the porous matrix of the pyrolysed source material until this ash fraction is washed out. This can also result in a reduction in pH, which impacts on metal[loid] mobility during the weathering of the sorbent in soils. Consequently, for a given sorbent material, there will be various mechanisms limiting the longevity of its effectiveness.

## The particular problem of arsenic

The metal[loid] arsenic (As) presents contrasting responses when soil amendments are introduced, both because it is present as an anion and because its solubility and mobility generally increase at higher pH. This presents a problem since a high concentration of As in soils at contaminated sites is often associated with the presence of heavy metals (for example mine sites, old smelting and metal-working localities). This means that

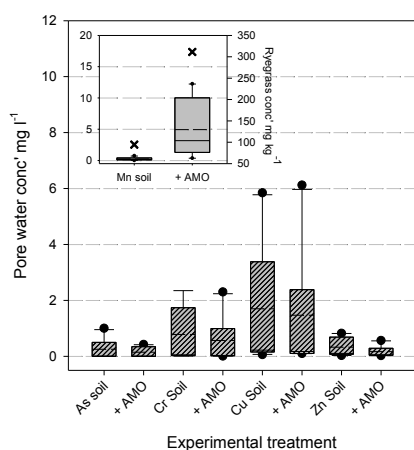
adding soil amendments which increase pH can liberate As into solution.

Iron (Fe) and manganese (Mn) oxide-based sorbents, whose positively charged surfaces attract As oxy-anions, have been successfully deployed to reduce arsenic mobility in soils and waters. Combining these metal oxides with organic-based sorbents has been trialled as a means of applying a 'one-stop-shop' sorbent for metal[loid] contaminated soil applications.

## Case Studies

### Case study 1: Mn-based amendment to a metal[loid] contaminated agricultural soil in UK

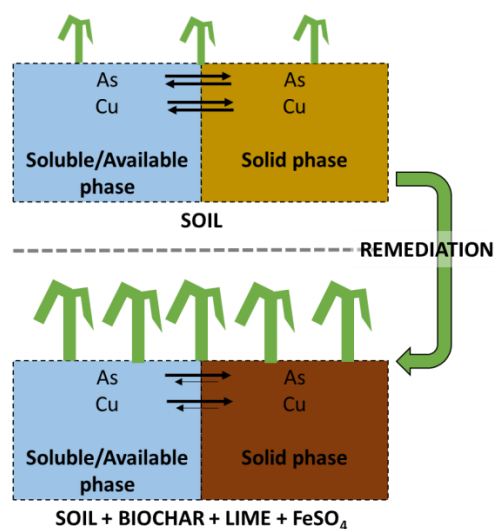
A coating of amorphous Mn-oxide on the surface of biochar produces a bio-sorbent with sites for anion and cation binding. This sorbent has been applied to three contaminated agricultural soils where As, Cr, Cu (from contaminated wood-ash application) and Zn (from contaminated sewage-sludge application) were present in high concentrations. In this laboratory pot test, pore water samples and ryegrass samples were analysed for metal[loid]s to determine their mobility and uptake, with and without bio-sorbent addition. Moderate reductions in metal[loid] concentration in pore water and ryegrass were achieved (Figure 2), but enhanced Mn leaching and uptake was also evident (Figure 2 inset), illustrating a potential limitation in the useful life of this sorbent in soil.



**Figure 2:** Mean (dashed line) and range of concentrations of metal[loid]s in pore water, as influenced by experimental bio-sorbent application. Inset shows Mn concentrations in pore water (box-plot) and ryegrass (crosses).  $n=10$ .

### Case study 2: Fe-based amendments to arsenic contaminated mine soil in Spain

A combination of iron sulphate, lime and organic amendments (biochar and composts) was applied to arsenic and copper contaminated mine soil which was subsequently sown with rye. The hypothesis was that organic matter would improve soil properties and retain metals, whilst a pH around neutrality would precipitate Fe oxides that were able to retain As. The co-applications of the three materials produced better plant growth, decreased metal availability and limited As mobilisation to a greater extent than individual applications (Figure 3). It proved important to maintain the pH between 6 and 7 because an excess or deficiency of lime caused either arsenic or metal mobilisation, respectively (4).



**Figure 3:** Schematic conceptual model of the effect of co-application of biochar, lime and iron sulphate to remediate a contaminated mine soil. Adapted from (4)

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# Modelling metal speciation in natural waters

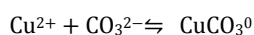
Stephen Lofts (NERC Centre for Ecology and Hydrology)

The behaviour and toxic effects of metals in natural waters are strongly impacted by speciation – the distribution of a metal among its different possible chemical forms. Computer models compute speciation at chemical equilibrium and are powerful tools if used with an understanding of their limitations.

The aquatic speciation of a metal refers to its distribution among its possible forms within a surface water. These forms include the free hydrated ion, complexes with small ligands such as carbonate, and with larger, chemically complex ligands such as humic substances, adsorbed on the surfaces of natural particles, and in mineral precipitates. There may be a number of chemical entities present in surface water which influence the speciation of a metal:

- i. Small inorganic ligands such as chloride (Cl<sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. Metals can bind to these ligands to form solution complexes;
- ii. Protons (H<sup>+</sup>), which will compete with metals for binding to ligands;
- iii. Other dissolved metal ions, such as calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), iron (Fe<sup>2+</sup>/Fe<sup>3+</sup>) and aluminium (Al<sup>3+</sup>), which will also compete with metals for binding to ligands;
- iv. Chemically complex dissolved ligands, particularly humic substances, which bind metals and protons as small ligands do, but which require complex modelling approaches;
- v. Chemically active components of suspended matter, including mineral oxides such as those of iron(III), manganese (IV), and clays;
- vi. In human-influenced waters, such as those receiving effluents from sewage treatment works, man-made ligands such as EDTA may be present in sufficient quantities to influence metal speciation (*J*).

The reaction of a metal with a ligand can be written quite simply, e.g. for the equilibrium between a copper ion and carbonate ion:



Here Cu<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> are the free (unbound) forms of copper and carbonate in water. The double arrow indicates that this reaction is reversible. At equilibrium, the relative concentrations of Cu<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup> and CuCO<sub>3</sub><sup>0</sup> will be constant:

$$K_{\text{CuCO}_3} = [\text{CuCO}_3^0]/[\text{Cu}^{2+}][\text{CO}_3^{2-}]$$

The term *K*, the equilibrium constant, can be found for a particular reaction by experiment. A chemical speciation model uses a database of equilibrium constants, for the reactions of metals, protons (H<sup>+</sup>) and ligands, to predict the speciation of the metals from the total concentrations of metals and ligands present. For example, the calcium (Ca<sup>2+</sup>) ions in water can compete with copper for binding to the carbonate ion:



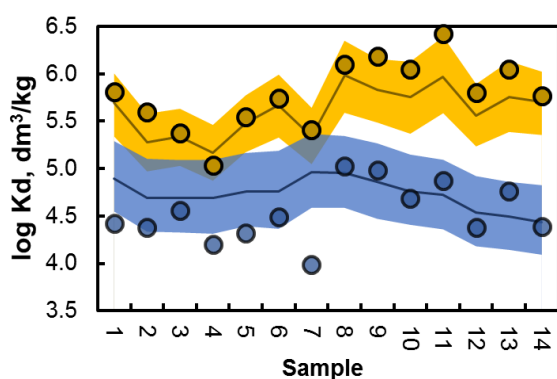
Given values of *K*<sub>CuCO<sub>3</sub></sub> and *K*<sub>CaCO<sub>3</sub></sub>, a chemical speciation model can automatically account for the competition between copper and calcium for binding to carbonate.

Metal speciation is important in understanding the transport of metal ions through surface waters and their potential effects on aquatic organisms. The extent to which a metal binds to ligands on the surfaces of suspended sediments, relative to its tendency to bind to dissolved ligands, will affect its tendency to be lost when the sediment settles out of the water – in lakes, for example. The uptake of potentially toxic metals by organisms is partly controlled by their speciation but also by competition with ions such as magnesium and calcium.

## Speciation in natural waters

A particular feature of natural waters is the presence of chemically complex ligands, both in dissolved form and on the surfaces of natural particles (sediments). These include humic substances, which are the dominant component of dissolved organic matter in natural waters, and minerals including oxides of iron(III) and manganese(IV), and clays.

Humic substances are formed from the breakdown of plant and animal matter. Their functional groups include carboxylic and phenolic acids and amines that are capable of binding protons and metals. Their chemical



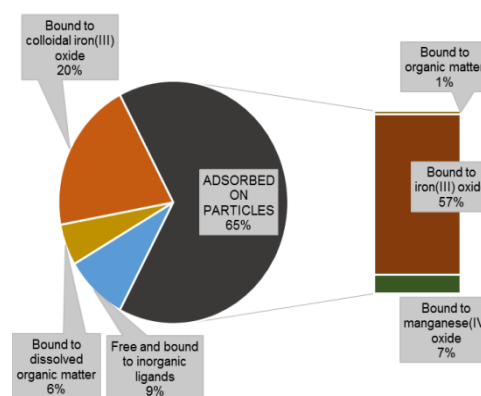
**Figure 1.** Observed and predicted partition coefficients,  $K_d$  for lead (yellow) and copper (blue) in a tributary of the River Ribble, north west England. The shaded areas show the uncertainty ( $\pm 2$  standard deviations) in the predicted partition coefficients. Data are from (5).

complexity arises from their heterogeneity: each molecule has a number of functional groups, each with its own chemical environment, so that they exhibit a range of metal binding strengths. Many of the functional groups can combine to form multidentate binding sites which have particularly strong metal binding affinities. Despite this complexity, sophisticated models for humic substances have been developed and are used in researching metal speciation in natural waters (e.g. 2,3). Minerals also have functional groups that bind protons and metals. The most important of these are oxides of metals such as iron(III) and manganese(IV), and aluminosilicate minerals, i.e. clays. Models have been developed for these substances (e.g. 4). They are commonly found in sediments, although they may also occur as colloidal particles. These may be small enough to pass through the filters typically used to separate 'dissolved' and 'particulate' materials in waters. Particles in surface waters may also contain other materials such as algal and bacterial cells which can bind metals (6).

Testing models against data from the natural environment tells us how well speciation measurements agree with the theory defined by modelling. Figure 1 shows an example of observed and predicted distributions of metals between solution and natural particles in a river. Such results can help us to assess aspects of the modelling, for example:

- Is the model as it stands useful in making predictions of metal chemistry in the field?
- Can we identify reasons why the model may perform poorly for some samples? Could it be due to uncertainties in the measured data, or could it be due to more fundamental issues that may require further model development?

A speciation model also makes more detailed predictions, for example about which ligand(s) metals are bound to. Figure 2 shows the predicted average speciation of lead. We can see that lead associates strongly with ligands, particularly iron(III) and manganese (IV) oxides. This includes iron(III) oxide, which is measured as 'dissolved', but is actually present as colloidal particles. This type of observation gives us insight into which measurements and model parameters are likely to be most important and allows us to target research efforts to improve models for the future.



**Figure 2.** The predicted average distribution of lead among its dissolved and particulate forms.

## General resources

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# Geochemistry and biogeochemistry of radioactive substances

Laura Newsome (Manchester University)

Anthropogenic radioactive substances can enter the environment from nuclear weapons testing, routine discharges from nuclear power plants and reprocessing facilities, mining and mineral processing, medical facilities and from nuclear accidents. Their environmental behaviour is controlled by whether they sorb to mineral surfaces, form complexes or colloids, or are subject to redox transformations – in the same way as their equivalent non-radioactive isotopes and metals in general. Crucially, all of these factors can be influenced by microbial processes and so understanding the biogeochemistry of radioactive substances is essential in order to predict their fate and environmental impact.

The most important radionuclides, in terms of their environmental abundance and radioactivity, are the actinides  $^{235,238}\text{Uranium}$ ,  $^{237}\text{Neptunium}$ ,  $^{238,239,240,241}\text{Plutonium}$ ,  $^{241}\text{Americium}$ , fission products  $^{137}\text{Caesium}$ ,  $^{90}\text{Strontium}$ ,  $^{129}\text{Iodine}$ ,  $^{99}\text{Technetium}$ , and tritium ( $^3\text{H}$ ).

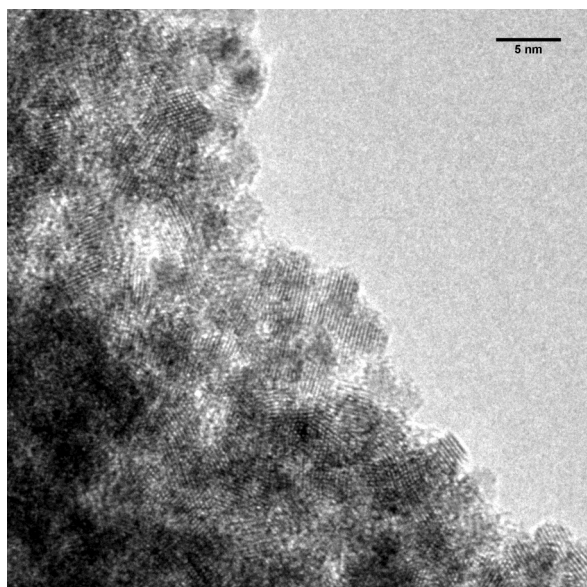
## Factors that Affect the Environmental Behaviour of Radionuclides

**Sorption to Mineral Surfaces:** Radionuclides can sorb to mineral surfaces through ion exchange, or the formation of inner sphere or outer sphere complexes. Ion exchange is the strongest form of sorption;  $\text{Cs}^+$  readily exchanges for other positively charged cations in the interlayer sites of illite, a common clay mineral, and over time this process becomes irreversible. The amount of sorption (or desorption) is pH dependent. Under acidic conditions, mineral surfaces become protonated which reduces their affinity for positively charged cations such as  $\text{Sr}^{2+}$ . Fungi are known to generate acidity by secreting organic acids, including oxalic acid, which can enhance

the dissolution of depleted uranium. Bacteria can also lower the pH of the environment by producing organic acids from the breakdown of complex organic matter. Some microbial processes can also cause the pH to increase, for example via denitrification (the reduction of nitrate to nitrogen) and ureolysis (degradation of urea to ammonium and carbonate), which allows the precipitation of  $\text{Sr}^{2+}$  in calcite ( $\text{CaCO}_3$ ). Although many radionuclides have been shown to sorb to microbial biomass, this is a temporary situation because the biomass eventually dies and decomposes, causing the radionuclides to desorb and become remobilised.

**Complexation:** In general, the complexation of radionuclides by ligands increases their environmental mobility. Complexing agents, including ethylenediaminetetraacetic acid (EDTA) and citric acid, are often used in the nuclear industry to decontaminate facilities. However, both Np and Pu ions are known to be more bioavailable when complexed to organic ligands such as EDTA. In the environment, uranyl carbonate complexes are highly soluble and have a lower electrostatic affinity to mineral surfaces compared to uranyl hydroxides. Natural organic matter in the form of humic or fulvic acids and fungal-secreted organic acids will complex radionuclides and increase their mobility. Microorganisms are also able to produce ligands that cause radionuclides to precipitate from solution as insoluble biominerals. For example, many bacteria use phosphatase enzymes to generate inorganic phosphate, and this can precipitate U from solution as autunite ( $\text{UO}_2\text{PO}_4$ ), whilst the sulfide produced by sulfate-reducing bacteria can precipitate Tc as  $\text{TcS}_2$ .

**Colloid formation:** Colloids are defined by IUPAC as molecules or poly-molecular particles dispersed in a medium that have, at least in one direction, a dimension roughly between 1 nm and 1  $\mu\text{m}$ . In environmental systems colloids behave as aqueous complexes and remain suspended in water where they are highly mobile and can be transported long distances. Colloids can be removed from the water column by sorption onto surfaces or by aggregation to form particles that precipitate. Radionuclides can form colloids, or sorb onto colloids of other materials such as clays, iron oxides and organic matter. Plutonium has been shown to be transported distances of more than a kilometre from nuclear sites when associated with colloidal particles.



**Figure 1.** Uranium(IV) biominerals produced by bacteria. Image credit: Laura Newsome.

**Redox transformation:** In general, redox-sensitive radionuclides are more soluble in their oxidised forms. U(VI), Tc(VII), Np(V), Pu(V) form stable oxycations (e.g.  $\text{UO}_2^{2+}$ ) or oxyanions (e.g.  $\text{TcO}_4^-$ ) that are mobile under the oxidising conditions typically encountered in surface waters and groundwater. However, under reducing conditions, they are sparingly soluble and tend to become associated with the solid mineral phase through sorption, or, if present at high enough concentrations, can precipitate as reduced phases such as  $\text{UO}_2$ . Microbial activity can affect the behaviour of redox-sensitive radionuclides by direct enzymatic reduction, that is microorganisms can gain energy from the reductive respiration of  $\text{U(VI)O}_2^{2+}$  to  $\text{U(IV)O}_2(s)$  coupled to the oxidation of organic electron donors. Alternatively, microorganisms can generate reducing conditions which cause the reductive precipitation of radionuclides. For example, microbial Fe(III) reduction is ubiquitous in the natural environment and the biogenic Fe(II) so formed can react with aqueous Tc(VII) to produce  $\text{Tc(IV)}_{(s)}$ , which can become incorporated into Fe(II) mineral crystal structures.

### Summary of Environmental Behaviour of Key Radioactive Substances

**Tritium:** tritiated water ( $^3\text{H}_2\text{O}$ ) is common and behaves identically to water. It can be incorporated into organic matter as organically bound tritium, which is more bioavailable than tritiated water.

**$^{137}\text{Cs}$ :** exists in the environment as  $\text{Cs}^+$  and does not form aqueous complexes in soil or water environments. It has a strong affinity with clay minerals, and substitutes for  $\text{Na}^+$  or  $\text{K}^+$ , becoming trapped in the interlayer sites.

**$^{90}\text{Sr}$ :** is mobile in groundwater as  $\text{Sr}^{2+}$  but can sorb to mineral surfaces through weakly bound outer sphere complexes.  $\text{Sr}^{2+}$  behaves similarly to  $\text{Ca}^{2+}$  and can become incorporated into the calcite mineral structure.

**$^{99}\text{Tc}$ :** is a common groundwater contaminant at nuclear sites and highly mobile as pertechnetate ion ( $\text{Tc(VII)O}_4^-$ ). It can be removed from solution by reduction to Tc(IV), mediated by Fe(II) generated by microorganisms, or by reaction with, for example, zero-valent iron.

**$^{129}\text{I}$ :** can be present in the environment as iodide ( $\text{I}^-$ ), iodine ( $\text{I}_2$ ) and iodate ( $\text{IO}_3^-$ ), all of which are stable and mobile. Soil microorganisms can volatilise iodide through methylation to  $\text{CH}_3\text{I}$ . Iodate can sorb to soils, but the development of reducing conditions can mobilise sorbed iodate as iodide.

**$^{235,238}\text{U}$ :** is commonly found in oxidising environments as highly mobile uranyl ( $\text{U(VI)O}_2^{2+}$ ) and uranyl carbonate complexes. U(VI) can be removed from solution by direct enzymatic reduction by microorganisms, by complexation with microbially-produced phosphate, and it can sorb to iron oxide minerals and natural organic matter such as peat. Fungi can transform depleted uranium to insoluble U(VI) phosphate minerals.

**$^{237}\text{Np}$ :** neptunyl ( $\text{Np(V)O}_2^+$ ) is highly soluble and exhibits limited sorption to surfaces. It can be reduced to insoluble Np(IV) by soil microorganisms and by Fe(II).

**$^{238,239,240,241}\text{Pu}$ :** plutonium has complex redox chemistry; Pu(V) and (VI) are considered to be oxidised forms, while Pu(III) and Pu(IV) are the reduced forms. All of these can be stable under natural environmental conditions. Pu predominantly associates with soils, sediments and particulate matter as Pu(IV). It is not readily desorbed from soils, and transport in the environment is primarily in colloidal form.

**$^{241}\text{Am}$ :** is present as Am(III) in the environment. It is stable over a wide range of environmental conditions and sorbs readily to sediments.

### Further Reading

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