RSC INTEREST GROUP
ENVIRONMENTAL CHEMISTRY

July 2023

Environmental Chemistry Group

Bulletin

This issue illustrates the many ways that chemists – analytical, environmental and educators – are tackling current concerns on the environment.

Book reviews: 'Greener' analytical techniques and the impacts of electronic waste are the topics for two new RSC books (reviewed p 4 and p 5).

Meetings: Water quality was the theme for our 2023 ECG Distinguished Guest Lecturer (**Professor Barbara Kasprzyk-Hordern**) and symposium (summarised pp 10-13). And we report on two of our successful symposia series, state-of-the-art analytical methods of complex environmental matrices (pp 7-8) and #EnvChem 2023 (pp 14-17).

Articles: Two articles discuss how to use anthropogenic carbon dioxide – as part of the circular economy (pp 18-21) and as a starting material for the construction industry (pp 22-24).

Environmental Briefs: Long-term radioactive geological storage and the environmental and toxicological problems posed by polystyrene nanoplastics are subjects for the latest ECG Environmental Briefs (pp 25-26 and 27-28, respectively).

Also in this issue: The challenge of explaining environmental chemistry to young children and the significance of environmental data to the general public are discussed by ECG committee members **Symiah Barnett** (p 9) and **Helena Rapp Wright** (p 3).

Contents

ECG Interview: Helena Rapp Wright 3

Book Review: Challenges in Green Chemistry, *by* *Roger Reeve* 4

Book Review: Electronic Waste Management, *by* *Laura Alcock* 5

Meeting Report : State-of-the-art in the analysis of complex environmental matrices, *by* *Roger Reeve* 7

Meeting report: Become a chemist for a day, *by* *Symiah Barnett* 9

Meeting report: Water, water, everywhere – is it still safe to drink? The pollution impact on water quality, *by* *Kiri Rodgers* 10

Meeting report: #EnvChem2023: Chemistry of the Whole Environment, *by* *Laura Alcock, Rowena Fletcher-Wood, and Helena Rapp Wright* 14

Article: The circular carbon economy and the future of carbon dioxide utilisation, ***by*** *Bhavin Siritanaratkul and Alexander J. Cowan* 18

Article: Transforming CO_2 into construction products, *by* *Colin D. Hills and Nimisha Tripathi* 22

ECG Environmental Brief No.37: Vitrification: Using thermal methods to increase long-term stability of geological disposal of radioactive waste, *by* *Lauren Harford* 25

ECG Environmental Brief No.38: The sources and impacts of polystyrene nanoplastics (PSNPs), *by* *Yifan Du* 27

ECG Bulletin

ISSN 1758-6224 (Print) 2040-1469 (Online). Published by the Royal Society of Chemistry's (RSC) Environmental Chemistry Group (ECG), Burlington House, Piccadilly, London W1J 0BA, UK.

See **www.envchemgroup.com** for articles published in the ECG Bulletin since 2007.

Environmental Chemistry Group

Website: www.envchemgroup.com
Twitter: @RSC_ECG
Facebook: RSCEnvironmentalChemistryGroup
Membership details: www.rsc.org/ecg

This and previous issues of the ECG *Bulletin* are available without charge at **www.envchemgroup.com** and **www.rsc.org/ecg**

Registered charity number 207890

Front Cover — Shutterstock Young woman is swimming in Lake Rannasee in Bavaria.

ECG Interview

The ECG Interview: Dr Helena Rapp Wright

(Imperial College London, h.rapp-wright@imperial.ac.uk)

Helena completed her PhD degree at Dublin City University (Ireland) in the School of Chemical Sciences in October 2021. Since then, Helena has been a Research Associate at Imperial College London (UK). Her research focuses on analytical and environmental chemistry, with expertise in contaminants of emerging concern and water analysis.

What inspired you to become a scientist?

I always enjoyed science in school. I remember the first time we visited a laboratory when I was in primary school – that set my mind early; it's the reason why I studied a chemistry degree. Also, when I was a kid, I loved watching series such as "CSI", and I was really determined to work in a laboratory! Years later, I graduated from King's College London (KCL) with an MRes in Forensic Science.

How did you come to specialise in water pollution?

During my MRes, I conducted a research project on how to detect and quantify trace organic explosives from wastewater samples; this acted as an early-warning sign for catchment areas in which explosives might be illegally manufactured, and led to my first publication. I enjoyed it so much, I knew I wanted to stay in water research. Later, I secured a PhD on different chemical contaminants in water, assessing environmental risk in different geographical locations.

Could you describe your current job?

Being a Research Associate allows me to explore different areas; from more environmental projects to public health, including determining contaminants in drinking water as an exposure route to humans. I collect samples and analyse them using different analytical techniques like LC-MS/MS, most of which I develop myself. I engage with different stakeholders and the public community.

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

Try different topics and get experience in different environments! Environmental chemistry has a broad set of applications; once you know the basics, you can move around the field easily, giving you opportunities to try different research and never get bored! I worked at the drug development services department of a company for two years between my Masters and PhD, and now I work at the School of Public Health.

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

Public engagement. It is hard to get the public interested in pollution work, without alarming them. Most sources usually have chemicals in really low concentrations (like a spoon of sugar in a swimming pool). While we shouldn't panic, we should also not ignore that these chemicals exist, as they may have negative impacts on the environment or our health.

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

When the public or a specific community are interested in your work and even volunteer to take part in a project, helping make a difference towards sustainability and a better environment in the future.

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

I can't think of anything else. I really enjoy what I do, but I guess I could have been a vet, as I love animals – or maybe an environmental lawyer!

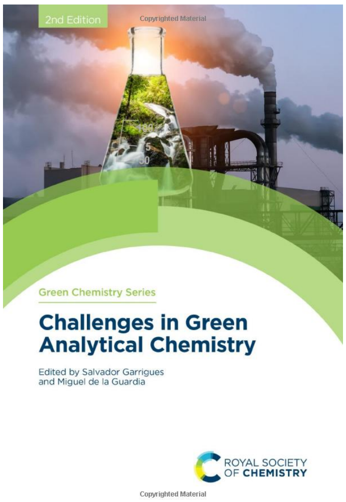
And what do you do when you are not working?

I love travelling and getting to know other cultures. I have currently visited 44 countries, and aim to reach 50 over the next few years! I also love food and trying new London restaurants (there is always a new place to go!).

Book Review

Challenges in Green Analytical Chemistry

Roger Reeve (rgrreeve@gmail.com)



Green analytical chemistry is the concept of making analytical chemistry safer for operators, more sustainable for the environment, and more economical.

Green analytical chemistry can involve choice of technique (including miniaturisation), sample pre-treatment, choice of solvents and reagents, or computer optimisation of procedure. Portable or handheld equipment may be available which would avoid the need for laboratory analyses. In this book, each chapter is written by a different author in the form of a detailed literature review. Examples are chosen from the whole area of chemical analysis with many details for environmental samples.

After an introductory chapter, the book continues with spectroscopic methods needing no sample pre-treatment, both invasive and non-invasive techniques, and also image analysis. The chapter covers the whole of the electromagnetic spectrum, mass spectrometry, and NMR, and so is sometimes difficult to follow, but provides a useful overview. It brings together many techniques overlooked in conventional chemical laboratories and includes a section on remote sensing.

The following chapter describes developments in biosensors, often in the form of simple, easily transportable meters. These have much application for personal monitoring in the biomedical field, but have currently more limited application for environmental samples as they are often for single analytes. Some developments are for less specific analytes, one cited being toxicity testing for wastewater treatment plants. Developments will expand the use of simple affordable techniques; *e.g.* colorimetric sensors using mobile phones and technology used in portable glycometers.

The major consideration of solvent choice is covered in several chapters, including not only conventional organic solvents but also alternative approaches such as solvent-free microwave extraction, supercritical fluids, ionic liquids, or near critical water extraction. A large section is devoted to miniaturised extraction techniques, including single drop microextraction and stir bar sorptive extraction. It concludes that many of the novel techniques have so far found limited widespread acceptance.

Two chapters are devoted to the specific areas of (bio) electroanalysis and flow analysis, introducing the techniques as tools for green analytical chemistry and describing current green developments; for instance, alternatives to mercury electrodes and replacement of hazardous chemicals.

Liquid and gas chromatography are discussed in a single chapter. Variations in technique such as two-dimensional chromatography, portable systems, online and at-line process chromatographs, and miniaturisation are included. Nevertheless, this chapter feels severely limited. Many of the techniques as used in cutting edge analysis would couple the chromatography to mass spectroscopic detectors with necessary chemometric processing of the vast amount of data produced. There is no discussion of this and, for instance, that recent advances in instrumentation reduce or remove the need for chemical pretreatment. A separate chapter on mass spectroscopic analysis would have been a very useful addition.

Chemometrics helps researchers in data manipulation, analysis, and automated information extraction. The chapter on this topic is a useful detailed summary of the methods used. Examples include analysis of PAHs and antibiotics in sediments, but the use of chemometrics in minimising environmental impact of analysis is not well highlighted, one of the most effective methods being in method design to reduce the number of samples needed.

The final chapter appraises the “greenness” of analytical methods, giving one example of DDT analysis in honey. It is only here that other vital aspects of any analytical procedure such as speed of analysis and limit of detection are considered. With such a general term, “greenness”, it is not surprising that results differ according to the criteria set.

This book is a good library of new methods for analysis and recommended for analytical chemists. However, in such a fast developing area, a final case study chapter on how green modifications are being applied in industry and existing long term monitory schemes would be welcome.

References

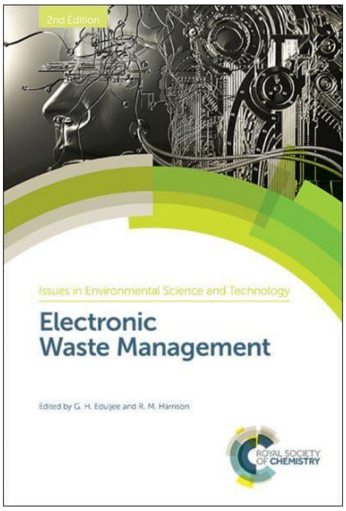
Challenges in Green Analytical Chemistry, ed. S. Garrigues and M. de la Guardia, Royal Society of Chemistry, Cambridge, 2nd Edition, 2020. ISBN 978-1-78801-537-0.

Book Review

Electronic Waste Management

Royal Society of Chemistry: Issues in Environmental Science and Technology Volume 49

Laura Alcock (Edwards Ltd, laura.alcock@edwardsvacuum.com)



2nd Edition

Issues in Environmental Science and Technology

Electronic Waste Management

Edited by G. H. Eduljee and R. M. Harrison

Royal Society of Chemistry

Electronic Waste Management is a 2020 update of the first edition (2008) of this book, and highlights changes in the perception of this topic between these two dates.

The introductory chapter summarises the scale of electronic waste, the directives and legislation around it, and discusses the composition of electronic wastes, available treatments and recycling methods and barriers to recycling.

The rest of the book moves from materials to circular economy methods, then to the management of electronic waste in different global economies and legislative environments. From here, the subjects explored are the potential methods for improving electronic waste management, and their various challenges.

The materials used in manufacture of electrical and electronic equipment (EEE) are explored in detail, as well as the directives driving materials changes. The first chapter sets a tone for the remainder of the book by describing factors that are barriers to sustainability of EEE manufacture and disposal. There is an interesting comparison of the three primary categories of waste EEE (WEEE) in households (mobile phones, televisions, and white goods) in terms of their recyclability.

The persistent distinction between new and "second-hand" devices does not fit within a circular economy.

The prevalent "take-make-waste" electronics system impacts on health, society and environment are highlighted. In particular, the dangerous working conditions arising from demand for resources and the poor legislative protection and practices in the countries where they are abundant are discussed. Further, the range of potential global e-waste value estimates after materials recovery (US$ 11.5bn – US$ 96bn) are compared, and the persistent distinction between new and "second-hand" devices identified as clashing within a circular economy. Cloud computing is explored as a step towards achieving a circular economy, with devices used only to access information. A summary of the Circular Strategies Framework is provided, and three primary strategies are identified, as well as potential potholes where designs could lead to planned obsolescence, rather than circularity.

There are reviews of the treatment of WEEE in the UK, Africa, and the Asia Pacific (APAC) region. The UK has consistently been the second largest producer of WEEE in Western Europe but fell short of its recycling and reuse targets consistently from 2014 to 2018 (the book was written in 2019).

A description of the Basel Convention is provided. This prohibits the movement of WEEE across borders; however, significant quantities are still shipped into African nations by concealing it amongst "used-EEE" that is sold to meet growing demand for devices. WEEE is the fastest-growing waste stream in Kenya and South Africa. An emerging narrative is identified of wealthier countries "dumping" WEEE on developing countries that do not have infrastructure or systems to process it in a safe and ecologically sound way, with methods used described as "hazardous to workers and the environment".

The chapter aptly titled "Broken Story about Production and Consumption" was particularly gripping. It highlights anti-trust practices utilised by electronics manufacturers, including planned obsolescence. It also indicates physical repetitive strain injuries, "psychological pain", and potential links between brain cancer and mobile use. This chapter also considers that "materials used for electronics are often selected on the basis of satisfying design needs, low costs, and high revenues and profits", with environmental aspects less important.

Chapter 9 is dedicated to batteries, potentially the most complex components within EEE. An overview of the variety of technologies and formulations is provided, along with the current (at the time of writing) volumes of recycled batteries versus the volumes of production. The legislation around batteries is then explored, including material handling regulations. Crucially, the legislation is intended to prevent heavy metals and other materials from polluting the environment, rather than emissions of carbon dioxide. This chapter draws attention to the increasing desire for longer usable life of batteries from manufacturers. Relevant to this is the fact that around 50% of "waste" lithium-ion batteries retain 70% of their nominal energy storage capacity. The overview of regulations around battery transportation and treatment explores the nature and processes of recycling batteries, with a particular focus on lithium-ion batteries. A clear statement is made that recycling the materials is "a complex and costly process hindered by the absence of a standardised product across the market".

The authors call to attention the need for emissions treatment in pyrometallurgy "from combustion of carbon and organic compounds", but do not explain why or what the emissions are. This becomes all the more concerning when reading the statement that "at the current time, pyrometallurgy is the overriding and dominant treatment methodology". Detailed, objective evaluation of some newly developed methods is provided. The chapter concludes that hydrometallurgy is needed to minimise the environmental impact of mining for battery materials, but that the resulting liquid pollution is currently unquantified.

Around 50% of "waste" lithium-ion batteries retain 70% of their nominal energy storage capacity.

The discussion moves on to novel design and process chemistries for the manufacture of printed circuit boards (PCBs), aiming to reduce the use of expensive or critical raw material and improving the end-of-life options, including repurpose and recycling. The global usage of copper, gold, and indium reserves makes for stark reading as the authors attempt to raise awareness of the need for their more efficient use in PCBs and recovery from end-of-life materials – the majority of which are already in landfill. To this end, there is an examination of alternative electrolytes being developed for chemical processing and coating of materials to achieve similar properties to those already established. Use of deep eutectic solvents (ionometallurgy) as solutions for metals recovery from PCBs is also explored. An application for this was noted in recovery of low concentration, strategic materials from photovoltaics, touch screens, and small magnets, etc.

The final chapter addresses the recycling of plastic itself, though the otherwise excellent editing seems to have fallen short here, as evidenced by the switching between tons and tonnes. The main issue is that "recycled plastics are still perceived as unattractive to the end-user". It goes on to summarise PolyCE circular business models, including how they function and what potential environmental benefits they offer.

An outline of the role of each group in the commercial chain, including retailers and end-users, is then presented. A comparison of the reuse of appliances based on collection points is also offered, with approximately 90% of appliances collected from households holding potential for reuse, but only around 1% from recycling centres. This drastic difference is explained simply by "this is often due to handling". It is noted that, however, designing a product to include recycled materials requires less investment than integrating recycled material into a complete product designed for production with virgin materials. There is also the clear statement that WEEE treatment operators need to improve their procedures, and recyclers need to improve performance of compounded plastic product to meet manufacturer specifications.

This book provides a great insight into the processes, challenges and progress around management of waste electrical and electronic equipment. However, some clarity is lost from the figures presented as a result of monochrome printing. Also, whilst each chapter starts with an abstract, the book may have benefitted from a chapter to summarise and conclude the collective works. The lack of such a chapter leaves a sensation that more needs to be said. However, the book is an excellent resource for anyone researching in the field of electronic waste management and should certainly be considered by anyone working in electronic equipment design and manufacture as food for thought.

References

Electronic Waste Management, ed. G. H. Eduljee and R. M. Harrison, Royal Society of Chemistry, Cambridge, 2nd edition, 2020. ISBN 978-1-78801-744-2.

Obituary. We regret to announce the passing of Mr Geoff Dickes, a member of the RSC's Environmental Chemistry Group and its predecessor, the Environment Group. Geoff was Chair of the Environment Group (1992-1993) during the time the Group's name was changed to the Environmental Chemistry Group. Geoff served as a Public Analyst for the County of Avon and was a pioneer in the application of gas-liquid chromatography for residue analysis (G. J. Dickes and P. V. Nicholas, "Gas Chromatography in Food Analysis", Butterworths, London, 1976). Geoff wrote a short account of the formation of the RSC's Environment Group for the first issue of the Environmental Chemistry Group Newsletter January 1995 (https://www.envchemgroup.com/pdf-bulletins.html). His full obituary may be found on the RSC website (https://www.rsc.org/membership-and-community/member-obituaries/2023/mr-geoffrey-james-dickes/).

Meeting Report

State-of-the-art in the analysis of complex environmental matrices

Roger Reeve (rgrreeve@gmail.com)

The fifth meeting in this biennial series discussed new developments in chromatographic, spectroscopic, mass spectroscopic, and data processing methods for analysis of complex atmospheric, aqueous, and solid environmental samples. The meeting was organised jointly by the Environmental Chemistry Group (Caroline Gauchotte-Lindsay, Roger Reeve), the Separation Science Group and the Water Research Forum (Graham Mills).

This year, the meeting had a new format, with four lunchtime webinars held fortnightly. Two speakers discussed topics in related areas, before discussion. This new format proved highly successful, with over 50 attendees at each session, the numbers slowly increasing during the course of the series.

The series was started by **Professor Barbara Kasprzyk-Hordern** (University of Bath) with 'Wastewater based epidemiology and One Health'. One Health is aimed at a holistic understanding and management of public and environmental health. The case study investigation looked at a whole catchment area on the river Avon, with five wastewater treatment plants and five towns/cities. It included monitoring 141 compounds of emerging concern. 75% of the population of 1.14 M was covered. Throughout the region, each person contributes around the same amount of chemicals per day (12 mg/day), but individual chemicals correlate with different populations. Temporal differences are also detected. Chemical concentration profiles can indicate a population's overall health. They may also indicate occupational exposure. Continuing work is developing means to identify specific chemicals and proteins that act as public health biomarkers.

The second speaker, **Dr Brett Sallach** (University of York), discussed 'Understanding the transport and fate of chemical pollutants in agroecosystems', focussing on the use of wastewater in agriculture with the possible uptake of pollutants by plants. Hydroponic experiments simplified the initial investigations by removing the effect of soil type. It was shown that bioconcentration correlated better with

water analysis than by soil type. Machine learning was then used to correlate uptake with chemical structure. Single-cell mass spectrometry (SCMS) is used to identify chemical residues and their metabolites in plants (see ECG *Bulletin*, July 2022, pp 12-13).

Two weeks later, **Professor Jacqui Hamilton** (University of York) began the second session with her presentation: 'Are emissions from green spaces important for urban air quality? Using high resolution methods to understand the interaction of biogenic emissions with air pollution in cities'. Reversed phase ultrahigh performance liquid chromatography with Orbitrap MS (UPLC with Orbitrap MS) was used to monitor the Beijing atmosphere over an extended period. The organic fraction is highly complex. The biogenic volatile organic compound (VOC) emissions impact the formation of ozone and secondary organic aerosol (SOA) formation.

Dr Leon Barron (Imperial College) followed with his presentation 'Rapid monitoring and risk assessment of chemicals of emerging concern at scale.' The need for rapid monitoring is necessary for schemes covering several hundred sites and potentially over a hundred analytes. The method used was direct injection into a liquid chromatograph with tandem mass spectroscopy (LC/MS/MS). The London catchment was monitored over a lockdown period. Sampling itself was achieved using citizen scientists who added local knowledge for the most ideal sampling sites. A separate investigation area was the development of a 3D printed passive sampler, providng a surrogate and more rapid method for analyte uptake by invertebrates.

In webinar three, **Dr David Scurr** (University of Nottingham) introduced us to 'Reducing combustion emissions with secondary ion mass spectrometry'. Here, he discussed how combustion deposits in diesel and petrol engines can reduce fuel efficiency. Analysis used Time of Flight (TOF) and Orbi Secondary Ion Mass Spectrometry (OrbiSIMS). Ion beams are fired at a specific area of the sample, and a structural depth profile built up. As well as the inorganic components, organic products from the lubricating oil may be found and complex polyaromatic hydrocarbons, their structure increasing in complexity with depth in the deposit. The presence of the complex molecules was confirmed using MALDI (matrix assisted laser desorption/ionisation).

Dr Nicholle Bell (University of Edinburgh) then spoke on 'Using NMR and FT-ICR-MS to tackle natural and man-made mixtures in our changing environment. A journey from peatlands to drinking water.' About 80% of UK's peatland is damaged by drainage. Major attempts are being made to reverse this. Can the changes be monitored analytically as the peat changes from anoxic waterlogged to dry conditions and subsequent restoration? Natural organic matter contains molecules in the range 200-500 Da, with many -OH and -COOH side groups. Peat core samples, water and NaOH extracts and pore water were taken. Solid state NMR of core samples showed changes of the average number of functional groups with depth, indicating a chemical correlation. Fourier Transform–Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) may be used for solid and liquid samples and so to compare the two phases and produce structural information. Multidimensional NMR (^{1}H, ^{13}C and ^{15}N) was also used. Specific structures were identified in the water samples. The techniques were then used in a separate investigation to determine structures found in the complex mixture produced when water, after several stages water treatment (and still containing residual organic material), is chlorinated.

The final webinar began with a talk by **Dr Richard Cross** (UK Centre for Ecology & Hydrology) on 'Monitoring microplastics in the environment – experiences in detection and interpretation of microplastic contamination in increasingly complex media. Microplastics arise from plastic degradation and may also be fibres beds and pellets. We need to identify a correlation between size/shape and adverse properties. No one analytical technique can cover the complete size range, the lowest range being flow cytometry, then μ-FTIR (Fourier Transform Infra-Red Spectroscopy), then ATR-FTIR (Attenuated Total Reflectance FTIR). Sampling itself may degrade the sample and data analysis affects the final result. The large differences found in literature results may be due to these considerations. Common principles and reporting requirements are needed to allow data from multiple sources to be combined and interpreted correctly.

Dr Mark Perkins (Anatune) finished the series speaking about 'Rapid analysis of soils and water using selected ion flow tube mass spectrometry (SIFT-MS)'. The technique is useful for small volatile organic molecules and some inorganic gases. It is transportable and has been used for field applications such as fenceline monitoring of industrial plants. Another advantage is its speed, several times faster than gas chromatography/mass spectroscopy (GC-MS) for volatile organics. Thermal desorption SIFT-MS is another application used for plastics or any other material which can produce volatile organics.

It seems fitting that, in a symposium series based throughout on 'New Developments', we should investigate using a new form of presentation. The overwhelming opinion was that the format and presentations were successful. If you missed any of these talks, or want to revisit them, they can be found on-line at:

https://youtube.com/playlist?list.=PLLnAFJx0jzZszpgJd_6Zhl-KFNZ-67IFL

Meeting Report

Become a chemist for a day

Symiah Barnett (Loughborough University, s.k.l.barnett@lboro.ac.uk)

Over the Easter holiday, I organised a one-day drop-in outreach project at Reading University entitled 'Become a chemist for a day'. The workshop comprised three main activities: a worksheet, an experiment, and an analysis exercise.

The importance of outreach for early career scientist

Researchers have highlighted the benefits of scientific outreach projects for both participants and scientists. They found participants gain enthusiasm for science as well as a greater understanding of the topic[1]. Additionally, scientists improve their communication skills, creativity, and develop the ability to show initiative[1,2]. These skills are import for early careers researchers, and outreach provides a platform for learning them. Despite this, research shows that only 40% of graduate students get involved in outreach on a frequent basis[2].

The activities

In the first activity, the students were taught about the five main branches of chemistry. The second activity was the analysis exercise: the students were given water from four different sources. The four sources were representative of sea, river, tap, and a washing machine water. Students were asked to determine the different sources through a series of experiments. The last activity involved creative experimentation, where the children wore laboratory coats and safety spectacles and posed for a photo dressed up as a scientist, whilst playing with the child friendly experiment kits and molecular model kits (Molymods®).

Turnout and outcomes

Overall, approximately 60 people attended, including 40 children. We used a questionnaire to evaluate the impact of the outreach events and to ultimately understand whether we achieved our aims. The core aim of this event was to stimulate the participants' passion for chemistry. This outcome was achieved and evidenced in the feedback form where one of the participants wrote the following: "The experience the girls had has provided them with a foundation to explore science. I was impressed with the organisation of the event. The experiments were engaging, and the children were happy to participate".

Personal reflections

This was an excellent learning opportunity for me as a PhD student, since it allowed me to learn about the grant writing process, helped me understand and handle university funds, plan an event, manage people, and communicate science to various audiences. I learnt that timeframes for organising events are often much longer than you first predict.

Figure 1. *Students learn about the five main branches of chemistry.*

I definitely recommend other early careers scientists engage with outreach.

References

1. G. Clark, J. Russell, P. Enyeart, *et al.,* Science educational outreach programs that benefit students and scientists. *PLoS Biology*, 2016, **14**(2):e1002368. https://doi.org/10.1371/journal.pbio.1002368
2. S.K. Rouzer, L.M. Kalinowski & E.T. Kaseda, The importance of promoting scientific advocacy & outreach for trainees. *Neuropsychopharmacology*, 2023, **48**, 713–715. https://doi.org/10.1038/s41386-023-01530-6

Meeting Report

Water, water, everywhere – is it still safe to drink? The pollution impact on water quality.

Kiri Rodgers (University of the West of Scotland, kiri.rodgers@uws.ac.uk)

The Environmental Chemistry Group's 2023 Distinguished Guest Lecture and Symposium was held on the 22nd of May at Burlington House. The event highlighted societal concerns over water quality and examined how we can monitor and regulate water standards to enhance environmental and public health. The ECG Distinguished Guest Lecture was given by **Professor Barbara Kasprzyk-Hordern** (University of Bath).

24 delegates attended in person and a further nine joined the online portion of this first hybrid Distinguished Guest Lecture event.

The symposium was opened by **Dr Stephanie Powley** (Environmental Chemistry Groups Website and Social Media Coordinator), who introduced the first speaker **Mr Rob Fryer,** who presented 'Rivers of life?'.

Through an extensive exploration of open water swimming and access, it was shown that open water swimming is a historical pastime, however, the quality of our waters is now being challenged.

The power of media was explored, particularly how false news has encouraged people not to swim in both dangerous and clean rivers. The dangers of wild swimming are extensive; however, many risks result from subsidiary land activities.

Mr Fryer highlighted his belief that the quality of the environment is intrinsically linked to the quality of life. Compared swimming in rivers to walking in Eryri (Snowdonia) National Park highlighting that eight people die every year walking here. But there is too much commercial interest to allow for the restriction of walking in Eryri, whereas river and lake swimming are more informal and less commercialised.

In 1999, Waterlog was published, by Roger Diken, where he coined the term "wild swimming". It was very much a term for swimming in lakes and rivers in the UK, but now it is just a denomination of swimming. At the release of the book, the populous took to wild swimming, enthusiastically.

The second speaker, **Professor Fiona Regan** (Dublin University), presented 'Monitoring pollution and its impact on water quality using innovative tools'. Here, we were

River and Lake Swimming warning signs from Rob Fryer's Rivers of life? Presentation.

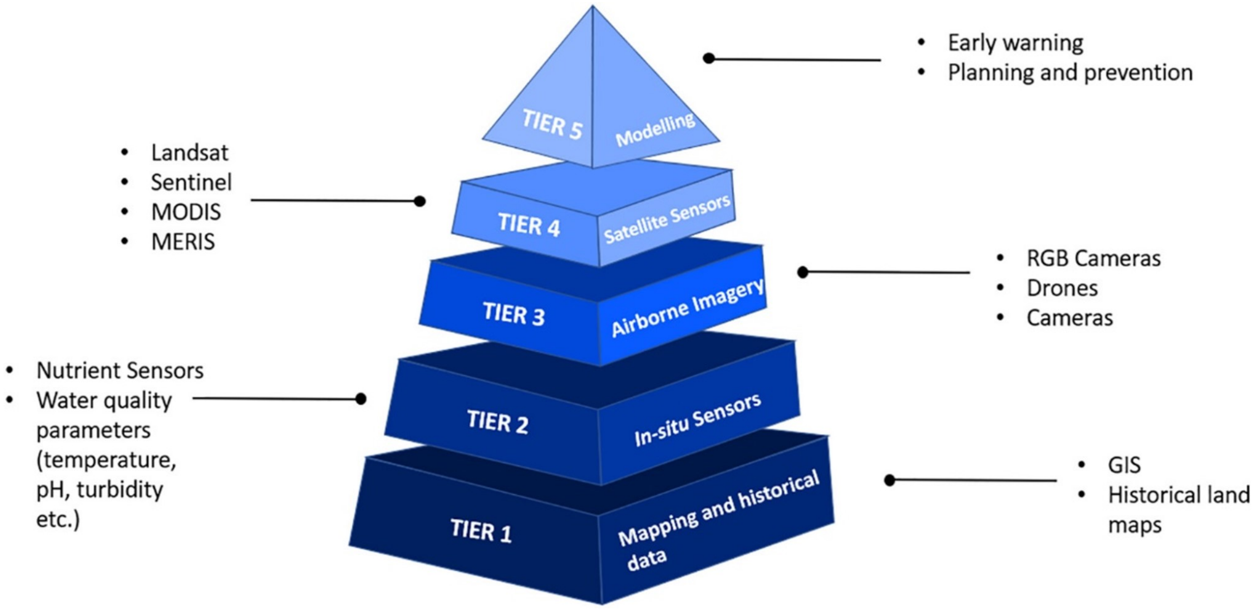


Diagram of the tiers of analytical methods and their benefits for water quality monitoring from Fiona Regan's presentation.

taken on a journey through water quality monitoring from the laboratory to the field; exploring how technology can lead to better decision-making to improve our environment. Professor Regan discussed the benefits of implementing sensors to gather multi-parameter information for water monitoring and management; how we can integrate these factors to inform management and prevention measures, and how emerging technologies can aid in combating climate change-related events (*e.g.* flooding and heat waves) as well as aiding in different sectors, such as aqua and agriculture (*e.g.* excessive algal bloom growth and phosphorus levels in waters).

By using technologies such as *in situ* sensors and satellites, Professor Regan's team plan to integrate a wealth of different data types to make these predictions. They have also been developing sensors for use in riverine systems for years, starting with tidal trends and looking at basic parameters such as pH, BOD and conductivity. An example was presented where Artificial Intelligence (AI) could predict events through hindsight studies, such as monitoring clusters of basic parameters such as dissolved oxygen, salinity, and temperature. These data showed fluctuations that resulted in an algal bloom in their watershed. If the team had been alerted by AI about warning fluctuations, they would have known to look at chloroform levels, and could have predicted the algal bloom.

She reported the development of a continuous fluorometric method for measuring E. coli (a measure of water quality from an ecological perspective). This technology was predicted to be used as a health alert device; however, more discussions are required for use in regulatory monitoring.

There was also potential to use these technologies for monitoring emerging contaminants, particularly organic compounds. These included pesticides, pharmaceuticals, personal care products, hormones, plasticisers, food additives, surfactants, and disinfectants. There are, however, analytical challenges. In order to take monitoring devices to carry out *in situ* analysis, a multidisciplinary approach is needed.

Professor Regan discussed her work on developing a bioassay in the field. Through the development of a cDNA analyser, the team applied an isothermal strategy to bypass Q-PCR requirements, and by using Cas12a single-stranded DNase activity, the team were able to utilise fluorescence detection for targeted interactions.

Other projects from Professor Regan's group include the identification of anti-depressants in water systems, and assessing the negative effects these drugs can have on the


A brief history of Water Regulation

- Public Health Act 1848
- Metropolis Management Amendment Act 1858
- EU water quality policy - absolute pollution limits for drinking and beach water
- Water Act 1989 / Water Industry Act 1991
- Water Framework Directive 2002
- Environmental Permitting Regulations 2016
- Environment Act 2021

Environment Agency

Dr John Collins presents a brief history of water regulation.

ecosystem. After a break for networking and coffee, **Laura Alcock**, Environmental Chemistry Group's Secretary and event organiser, introduced the third speaker, **Dr John Collins**, a Deputy Director in the Chief Scientist's Group at the Environment Agency in England. Dr Collins presented 'Regulating for the Water Environment'**,** highlighting the importance of combining these two processes, and giving us a history of water regulation, where our current framework is, and what challenges we face.

> **By looking at the bio-chemical life cycle, we discovered the impact on a global scale, which confirmed the lack of boundaries when pollution is concerned.**

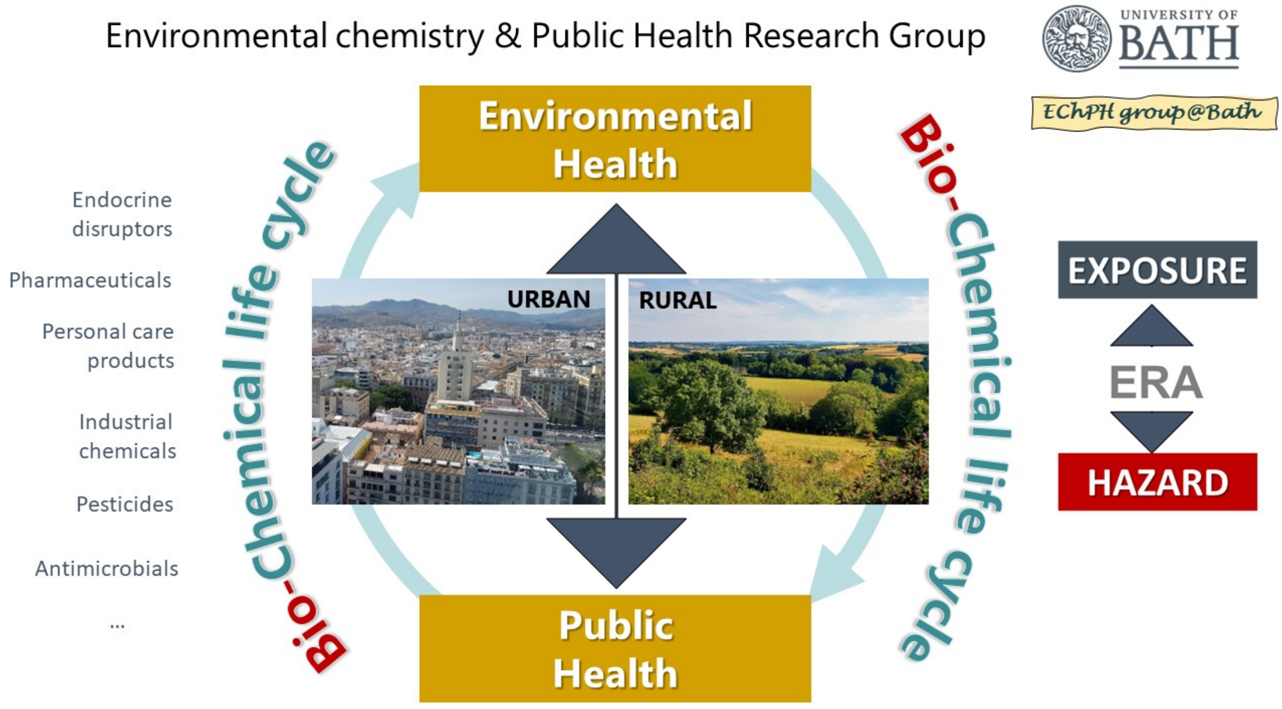
With current news often highlighting the impact of river and coastal pollution, Dr Collins discussed the importance of regulation and its associated aspects such as legal requirements, advice and guidance, incentivisation, permitting, compliance, enforcement, and non-regulatory partnerships, for an improved future.

Currently, the Water Framework Directive (WFD) and river basin management plans go hand in hand to improve water quality in the environment. Although just 14% of English rivers are considered "ecologically Good" according to the WFD, there are a range of parameters that state otherwise, *e.g.* individual tests (with 77% passed), ammonia and invertebrate levels are on the rise. It is also important to note that this approach does work with a significant reduction in serious pollution incidents, down from over 500 cases in 1995 to less than 100 in 2021. This is further reflected in an increase in the "excellent" status of bathing waters.

There remains a struggle to meet targets due to anthropogenic activities such as physical modifications, wastewater production, agricultural and rural land activities, and the introduction of non-native invasive species. This, combined with additional challenges such as ageing infrastructures, climate change, population growth, and cost of living, has driven the EA to implement further policies. This includes a 25-year environmental plan: the Environmental Act 2021, Environmental improvement plan, and integrated plan for water (published by DEFRA) – where they hope to "develop a suite of new policy interventions designed to transform how we manage the water system in a holistic way".

With agriculture considered one of the largest contributors to water pollution, the EA has taken steps to try to combat this, including through increased inspections, incentive schemes such as silage stores, and by working with local task forces.

Our 2023 Distinguished Guest Lecture was delivered by **Professor Barbara Kasprzyk-Hordern**, whose research focuses on interrelated areas of the environmental, analytical and water sciences. Combining these three disciplines, Professor Barbara Kasprzyk-Hordern reviewed her work on 'water fingerprinting' for assessments of environmental and public health. By looking at the bio-chemical life cycle, the impact of pollution on a global scale, irrespective of national boundaries, is revealed. Importantly, there was a need to discover how this impacted humans directly, and Professor Kasprzyk-Hordern discussed the advantages of using wastewater-based epidemiology.



Environmental chemistry & Public Health Research Group

UNIVERSITY OF BATH

EChPH group@Bath

Endocrine disruptors

Pharmaceuticals

Personal care products

Industrial chemicals

Pesticides

Antimicrobials

...

Environmental Health

URBAN

RURAL

Public Health

Bio-Chemical life cycle

Bio-Chemical life cycle

EXPOSURE

ERA

HAZARD

Biochemical life cycle slide from Barbara Kasprzyk-Hordern's presentation.

This process provided a comprehensive, continuous, anonymous, near real-time approach that ensured objectivity and unbiased results. Such research demonstrated the ability to map the spatial and temporal distribution of specific drugs or chemicals at a community level. This, in turn, could inform key stakeholders through a One Health approach, which included mixing different sciences (natural, social, medical and engineering), locations (*e.g*. Europe, Africa, America, Asia), and industrial sectors (NGOs, Government, Industry).

Professor Kasprzyk-Hordern explained how a One Health framework can provide a holistic evaluation process of combined community and environmental risks. She demonstrated multiple case studies in which water treatment works were perfect model systems that influenced water quality. Her team were also able to select sampling sites which would, in turn, enable them to represent the output of different chemical groups from a community level.

Through extensive analysis, Professor Kasprzyk-Hordern examined a current global issue – antimicrobial resistance. Research to date shows through resistant gene identification, the endemic correlated to communities, as opposed to antibiotic levels within the surrounding environment. This suggested that there are other drivers for resistance such as activities related to specific communities, for example, agricultural, urban, or rural settings. It is suspected that there is an issue in that the fluctuations of these two aspects (antimicrobial resistance and community activity) are set in different timescales. Antibiotics showed short-term variations, but antibiotic resistance genes showed much longer-term trends and variations.

The question was raised over whether Bisphenol A exposure is really below threshold levels, as samples are not taken from the requisite representative thousands of individuals. WBE supported the analysis of this.

Biomarkers rather than BPA were measured in the wastewater to determine how much of the material present was there as a result of human/animal exposure to BPA.

This approach can also enable identification of exposure markers through daily loads. Genetic markers were the most informative, with "hot spots" of infection showing that different communities suffer from different infections at different times. This information could help to deliver rapid response strategies, and also provides the basis for tackling future pandemics. A problem aspect of this process is that it is incredibly data heavy, making it both time-consuming and costly. However, the hope is that these discoveries will enable a cost-effective monitoring process that can combat antimicrobial resistance, climate change and many more global events.

This talk concluded a thought-evoking day of science and highlighted the importance of a one-health approach being required for future environmental security.

Laura Alcock presented Professor Kasprzyk-Hordern with the Distinguished Guest Lecturer's medal and opened the floor to general discussion before closing the event.

DGL Medal presented to Prof Barbara Kasprzyk-Hordern.

Meeting Report

#EnvChem2023: Chemistry of the Whole Environment

Laura Alcock (laura.alcock@edwardsvacuum.com),
Dr Rowena Fletcher-Wood (rowena.fletcherwood@gmail.com),
and Dr Helena Rapp-Wright (h.rapp-wright@imperial.ac.uk)

#EnvChem is an annual two-day international event where environmental chemists share developments across environmental chemistry. In 2023, it was held at the University of Glasgow on June 1st and 2nd, and featured four keynote speakers, 25 oral and 22 poster presentations. The meeting was organised by **The Royal Society of Chemistry, Environmental Chemistry Group**, the **BMSS Environmental and Food Analysis Special Interest Group**, and the **UK Branch of SETAC.**

Our initial and most popular session, pharmaceuticals in the environment, was chaired by **Dr Caroline Gauchotte-Lindsay** and **Dr Helena Rapp Wright**.

Our opening keynote speaker, **Professor Sharon Pfleger,** (NHS Highlands) provided an introduction to antimicrobial resistance (AMR) in her talk 'From bench to impact – making a difference in environmental chemistry research', particularly noting the prevalence of the problem over the solutions/impact in the field. She and her team received a novel grant for their work towards revolutionising prescribing practices, improving environmental risk assessment, and contributing to sustainability targets through expanding pharmaceutical environmental data. They aim to include this alongside clinical and cost-effective information to support prescribers in choosing between drug alternatives. Professor Pfelger wrote an excellent post about her keynote talk on LinkedIn: https://www.linkedin.com/feed/.update/urn:li:activity:7072887252690821120?updateEntityUrn=urn%3Ali%3Afs._feedUpdate%3A%28V2%2.Curn%3Ali%3Aactivity%3A7072887252690821120%29

Gabriele Frascaroli (Glasgow Caledonian University) presented 'Occurrence of antibiotics responsible for the development of anti-microbial resistance in wastewater treatment plants and their removal via microalgae'. He shared novel data on active removal and biosorption results in microalgae, and discussed the differences in these mechanisms, which depend on the nature of the target antibiotics. Uptakes up to 96% were achieved. Efforts continue to improve the systems and explore other microalgae.

Mazumdar-Shaw Advanced Research Centre, University of Glasgow (#EnvChem2023 venue).

Kemi Oloyede (Imperial College London) followed with 'Measurement and in silico prediction of pharmaceutical biotransformation in receiving water', with a focus on pinpointing worst affected contaminated surface waters (which tend to be close to wastewater treatment plants) and modelling retention time to identify potential chemicals alongside screening techniques for suspect compounds such as vaccine transformation products using LC-QTOF-MS.

Hamed Rasouli-Sadabad (Ulster University) discussed 'Antimicrobial resistance spread during antibiotics removal from water by adsorption' with a remarkable focus on disadvantages of adsorbents in wastewater treatment. He demonstrated a huge increase in horizontal gene transfer by introducing activated carbon, and used modelling to explore mechanistic steps.

Tathagata Pal (Indian Institute of Technology Bombay) delivered 'Handheld cost-effective optical fibre biosensor for detection of ciproflaxin and enrofloxacin in environmental samples with optical setup miniaturised into a µSense device'. The device was successfully tested both in India and Scotland, detecting antibiotics as low as 1 ppb in various surface waters.

Dr Lydia Niemi, (University of the Highlands and Islands) presented 'Innovative data visualisation tool to

#EnvChem2023 Delegates at the evening community building event at the Clydeside Distillery.

explore relationships between pharmaceutical prescribing and environmental occurrence', highlighting the fundamental principle of the One Health Breakthrough Partnership: human, animal, and environmental health inter-connectedness. Critically, her work includes a gap analysis which determined that rural areas were not frequently monitored. Environmental data were linked to high granularity prescription trends to create an interactive online tool for quick review of vast volumes of data.

Deborah Reid (Glasgow Caledonian University) covered 'Analysis of antibiotic and heavy metal contamination in wastewater to assess contribution to antimicrobial resistance'**.** She demonstrated the development and spread of AMR using a 60 x 120 cm agar plate visual, and discussed analysis of antibiotic and heavy metal concentrations in wastewater and biofilms, including identification and quantification of AMR genes across each of the four seasons.

Emma O'Sullivan-Carroll (University College Cork) gave a talk on 'Development of greener analytical methods for the detection of active pharmaceutical ingredients in wastewater effluents using capillary zone electrophoresis', which offers a fast (< 10 minutes) method for detection of antibiotics. The method benefitted from "greenness" (producing less organic solvent waste). Resolution and standard error were also compared with HPLC.

Alexandra Richardson (Imperial College London) spoke on 'The IMPART project, a citizen science approach to using passive samplers to monitor for emerging contaminants', using a newly separately multi-sorbent 3D printed passive sampler. Analysis of samplers from communities across a wide geographical catchment revealed similar concentrations of emerging contaminants except near wastewater treatment plants. Personal care products dominated the contaminants. The team is now looking to improve their citizen scientist provision.

The in-person event included a dedicated poster session. This included soil science explorations of:

- Novel characterisation and soil regeneration with accelerated carbonation (AC).
- Trace analysis of perfluorinated alkyl substances (PFAS).
- Elucidating biochemical mechanisms suppressing decomposition in peat soils via DNA extraction without soil organic matter (SOM) contamination.
- Modelling sorption dynamics of AMR-promoting drugs on mineral surfaces.
- TGA-FTIR for simultaneous assessment and quantification of contaminants and carbonation.
- The behaviour of small molecules in soil ecosystems using 3D printed personal sampler devices (PSDs).
- Molecular chemical processes behind soil ecological services and the Tea Bag Index (TBI) citizen science initiative.
- Fungi nutrient cycling via steroid alcohol conversion into biomass.
- Electrochemical biosensors for environmental monitoring applied in fungi.

In aquatic environments:

- Spatial distribution of perfluorooctanoic (PFOA) and perfluorooctanesulfonic acids (PFOS).
- Epidemiology of heroin-use across 9 English sites.
- Low-molecular-weight-gelator (LMWG) gels for circular remediation approaches to emerging contaminants.
- Assessing concentrations, spatiotemporal trends, annual fluxes, and sources of pharmaceuticals.
- The effect of natural organic matter (NOM) sorption in decreasing toxic micropollutant extraction by granular activated carbon (GAC).
- Optician sensors for sustainable, scalable monitoring mimicking biological "tasting".

Gas analysis focused on:

- Novel electrospun nanofibrous NiFeAl layered double hydroxides, offering novel recyclability with PVA-bases, uniform pores, and enhanced flexibility.
- Monitoring volatile products of incomplete destruction (PIDs) from PFAS removal technologies.

In mixed matrices, presenters demonstrated:

- Sample preparation and analysis of spiked liquid and solid matrices.

- Monitoring pyrethroid pesticide/insecticide levels in environmental and biological matrices.
- The gap in suitable, recognised methodologies for tyre and road wear microplastic analysis.
- PFAS content of complex food matrices.
- Evaluating the effect of storage and packaging on the volatile composition of beverages.

In the session on legacy and emerging contaminants, chaired by **Dr Peter Baugh**, **Professor Andrew Hursthouse** (University of the West of Scotland) introduced 'Resource exploitation and environmental impact: challenges from China's rapid industrial expansion'. He examined the impact of mineral extraction on concentrations of harmful heavy metals like arsenic in localised land and crops, demonstrating a strong correlation with rice crops. Remediation policy is still developing.

Dr Laura McGregor (SepSolve Analytical) spoke on 'Non-target screening of polar organics in cigarette leachate by immersive sorptive extraction and GC×GC–TOF MS' primarily via sorptive extraction. Approximately 4.3 trillion cigarette butts are estimated to end up in the environment, a toxic plastic containing ~7,000 toxic pollutants. A non-target GCxGC-TOF-MS approach successfully identified chemicals in leachate including nicotine-containing compounds.

4.3 trillion cigarette butts are estimated to end up in the environment… containing ~7000 toxic pollutants

Dr Mark Barrow (University of Warwick) spoke on 'Tracking the history of polycyclic aromatic compounds in the River Thames estuary using Fourier transform ion cyclotron resonance mass spectrometry'. This talk discussed the use of FTICR-MS to categorise petroleum compounds, which present challenges in their complexity for sample preparation and data output volume; however, they can be incredibly useful for analysis of complex materials and matrices such as petrochemicals.

Dr Keng Tiong Ng (Imperial College London) spoke on 'Development of a rapid LC-MS/MS method for explosive substances in complex matrices'. Approximately 15% of terrorist threats come from bombing attacks. Wastewater epidemiology approaches may provide crucial early warnings. In this talk, a new "direct injection" (no pre-treatment) LC-MS/MS approach was presented to detect and quantify 29 explosives from environmental samples.

Our final keynote speaker of the day was **Dr William Peveler** (University of Glasgow) presenting 'From water to whisky: golden opportunities in analysis with plasmonic particles', where he employed Au optical nanosensors to find patterns in and to categorise treated and untreated water chemistries. Extending this work, he applied the analysis to rapidly find chemical congener trends in whisky samples. Could this be used for fraud detection and augment human tasting panel analyses? Age comparison showed a correlation to rate of Au NP production, but correlation to other techniques varied.

Day two began with a online keynote speaker by **Emma Holland-Lindsay**,(National Federation of Women's Institutes). The WI, who act as a women's education group, equality advocate, and campaign pressure group, first raised awareness of household microplastics, including how a single clothes wash releases up to 13,700 microfibres, in 2016, launching 'End plastic soup – The Women's Institute's campaign to tackle microplastic fibre pollution'. "The term microfiber had not been mentioned in parliament in relation to plastic pollution prior to 2016", but since occurred in over 50 discussions. Alongside working with MPs, and craft demonstrations, the WI generated a 2021 report summarising six top tips for reducing microplastic pollution, and helped to secure research funding.

The session on microplastics, chaired by **Laura Alcock,** featured talks from **Dr Gideon Idowu** (Federal University of Technology Akure) with 'Microplastics and plastic-related organic contaminants in Africa's freshwater and marine environments'. Environmental laws in Africa are poorly enforced, leading to a high contribution of global marine plastic pollution, as illustrated with freshwater and sediment samples from eight African countries, where phthalate esters and phenolic compounds were found at high environmental concentrations.

Dr Louise Hamdy (CGG) spoke on 'High-throughput screening of sediments for microplastic pollution: adapting an automated mineralogy approach'. The talk highlighted the complexity of analysing soils and sediment matrices. However, techniques such as quantitative evaluation of minerals by scanning electron microscopy offers faster, more efficient screening, especially for samples of microplastics of different shapes and sizes.

Peter Hollings (Coventry University) spoke on 'Assessing the retention of new and emerging pollutants in nature-based Solutions by online SPE LC-MS and µFTIR microscopy'. A treatment train constructed at Coventry University Ryton Organic Gardens tested samples for five different persistent contaminants, including antibiotics such as amoxicillin; all were below the limits of detection. However, different microplastics were detected in all samples including some from tyre rubber.

Our soils system session, chaired by **Dr Carla Comaran Casas**, began with 'PFAS distribution in contaminated soils and impact on rhizosphere and plant microbiota' by **Dr Lucia Rodriguez-Freire** (Newcastle University). PFAS are highly persistent due to high chemical, thermal and biological resistance, and accumulate in plant roots, stems and shoots. The talk discussed analysis compounds taken up in plants and soil, studying retention and mobility.

Despite recommendations for low limits of these “forever chemicals”, there are no specific regulations in Europe.

Dr Claudia Rocco (Imperial College London) covered her ‘Investigation into stability of micronutrient complexes with PDMA, a novel ligand as fertiliser'. She reported a new synthetic ligand that may stabilise the delivery of nutrient metals such as iron and zinc. Use of the ligand increased uptake concentrations of iron, but not zinc, although both demonstrated strong chelation and logK values that compared well with those of natural ligands.

Niall Marsay (Cranfield University) shared ‘Development and optimisation of rapid analysis of weathered slag using portable XRF’**.** Brownfield sites (primarily industrial revolution) potentially rich in legacy contaminants present an ongoing issue. Handheld X-ray fluorescence (XRF) spectrometers offer fast, extensive analysis, shown with weathered slag from former metallurgical sites, including at Europe’s former largest blast furnace.

Dr Nitin Khandalwal (Imperial College London) started our sessions on water treatments, chaired by **Dr Baptiste Poursat**. He spoke on ‘Engineered iron nanostructures on different surfaces for continuous water purification'. Removing potential contaminants from water is crucial to address increasing global water scarcity, but remains a challenge. Nano-enabled approaches for aqueous decontamination were discussed, such as redox-active iron composites for degradation. In a circular economy approach, this was paired with sustainable nanoparticle recovery.

Bence Solymosi (University of Leeds) addressed ‘Disentangling adsorption from true catalytic degradation in advanced oxidation processes’, highlighting the problem of competition between absorption and true catalytic degradation. Experiments on carbon and oxidised carbon beads showed different removal percentages and significant changes in surface chemistry.

The afternoon keynote speaker, **Dr Salim Alam** (University of Nottingham) spoke on 'Oxidation chemistry in the atmospheres of global megacities’. In extreme urban environments, life expectancy may be reduced by 2.5 years due to particulate pollutants. Research included real time monitoring across London, Beijing, and Delhi, modelling, ~1200 filters, and offsite analysis, as well as PM visualisations demonstrating PM2.5 concentrations (µg/m^3) in Delhi significantly higher than WHO 2021 guideline limits. Sources of metal contamination included unregulated extraction. Challenges in experimental set-up involved cages to prevent monkeys eating inlet lines.

Dr Rowena Fletcher-Wood chaired the final session on indoor and outdoor air, featuring **Dr Amber Yeoman**, University of York, who explored the 'Atmospheric fate of consumer products’ – the neglected environmental fate and their impact on indoor air quality. Volatile organic compounds (VOCs) from consumer products are a major air pollutant, but give numerous chemical profiles, even for similar products, and data are scarce: air pollution is not a focus of “green” consumer products, especially non-aerosols, a challenge to improving indoor and outdoor pollution and atmospheric fates.

Holly Walder, Imperial College London, covered ‘Development of low-cost miniaturised passive air samplers for measuring (semi) volatile organic compounds in personal, indoor and outdoor environments’, addressing concerns about the redevelopment of UK brownfield sites, by investigating different chemical fingerprints using passive air samplers deployed in indoor and outdoor environments, where VOCs were detected such as TCIPP, a flame retardant. The community living close to the investigated areas was heavily involved in the research methodology and aims.

Jessica Gabb, IS Instruments, discussed ‘Measuring natural gas with Raman spectroscopy’, where she illustrated technological efforts to amplify gas phase Raman signals. Proof-of-concept work involved compromises between fibre length, fill time, and counts to identify detection limits (a few µL of sample, 2 ppm with a 15 m fibre). New research is investigating the possibility of using multi gas channel when using the same device.

Thomas Warburton, University of York, completed the talks with ‘The effect of ventilation on exposure to indoor VOCs in Bradford’. VOCs can leach into the surface, an example of source is outdoor air including cooking, one of the top sources. There is emerging evidence which shows ventilation rates may impact changes in long-term indoor VOC concentrations.

Prizes were awarded to **Louise Hamdy**, **Dr Nitin Khandelwal**, and **Holly Walder** for their outstanding oral presentations; and to **Dana Druker**, **Abdullah Shahid**, and **Sophie Singer** for their outstanding poster displays.

Our committee, speakers and delegates have been very active on social media during the conference; search for **#EnvChem2023** to get a further feel for the event!

Poster winners with the Prize Committee.

Article

The circular carbon economy and the future of carbon dioxide utilisation

Bhavin Siritanaratkul and Alexander J. Cowan

(University of Liverpool, acowan@liverpool.ac.uk)

Carbon-containing product streams need to become more circular, embracing the use of wastes as resources. Using renewable electricity, waste CO_2 can be converted into valuable fuels and chemicals in a process called electrochemical CO_2 reduction. Here, the technological barriers and the outlook for the scaling-up of process are outlined.

Circular resource flows

There are many definitions for circular economy, which has substantial overlap with related concepts, such as "green chemistry" and "sustainability"[1]. Some processes can follow principles of green chemistry (*e.g.* atom economy, safe components, easily degradable waste) while still using resources in the linear fashion of "take-make-dispose" (see **Figure 1**). Here we use a working definition that a circular economy aims towards decreasing new resource extraction whilst maintaining resources already in use and reducing waste generation and, in the case it cannot be reduced, the waste can be used as a resources.

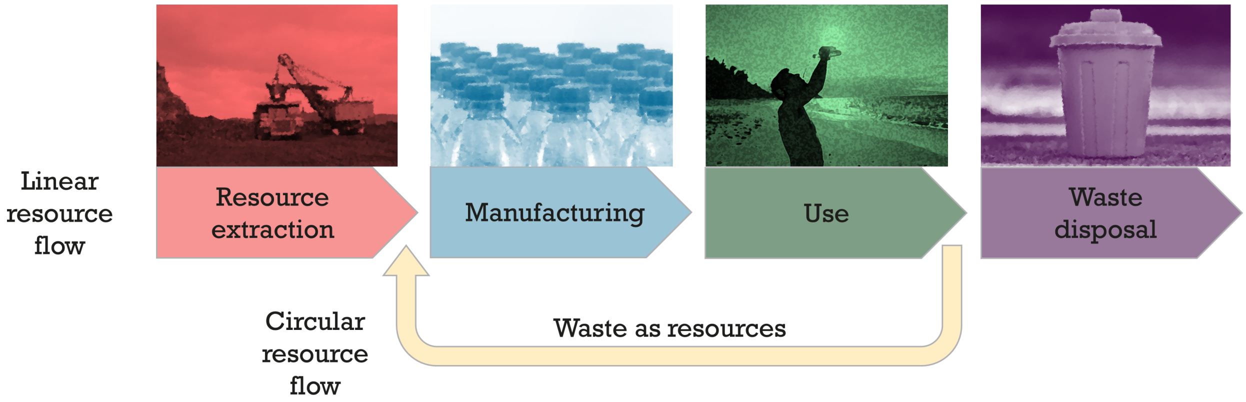


Figure 1. *Linear and circular resource flows.*

The UK has recognised the importance and urgency of implementing a circular economy and, in 2021, UK Research and Innovation (UKRI) initiated the largest investment to date in this area by creating five Research Centres, each focused on a certain resource. As part of the UKRI Interdisciplinary Centre for Circular Chemical Economy, we focus on the circular use and production of olefins (unsaturated hydrocarbons). The other Centres work on textiles, (bulk and technology) metals, and construction materials. In addition to these resources, nitrogen and phosphorus (N- and P-) containing chemicals are also vital resource streams that need to become more circular.

We focus on the circularity of carbon-containing resources (olefins) because:

1) Olefins represent more than 70% of industrial organic chemical production, since they are the feedstocks for manufacturing of plastics as well as rubbers, solvents, and surfactants;

2) The main source of olefins is petroleum, which is non-renewable;

3) Carbon-containing waste (CO_2, and to a lesser extent methane, CH_4) is the main driver of global warming, and olefin production and manufacturing gives rise to 32% of total CO_2 emissions from the UK chemicals sector.

CO_2 utilisation

If we were to consider waste CO_2 as a resource, it would be advantageous to use a concentrated waste stream, such as from power generation or industrial processes. Looking at CO_2 emissions by sector, electricity and heat generation accounts for 42.7% of total CO_2 emissions, and manufacturing and industry combines for another 21.4%[2]. This suggests that majority of CO_2 emissions can be potentially captured, converted, and reinserted into the resource stream, provided there is an efficient process using renewable energy as the input.

What sort of products can we aim to generate from CO_2? Broadly, the products of CO_2 conversion can be categorised by the number of carbon atoms as C_1 and C_{2+} molecules. C_1 products include carbon monoxide (CO), formic acid,

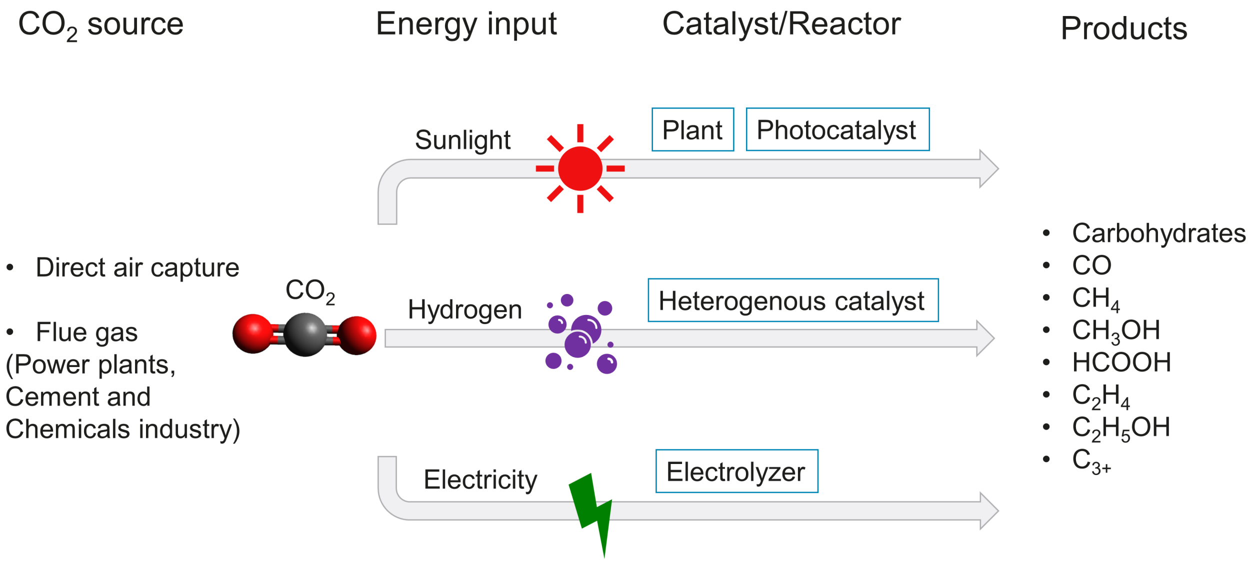


Figure 2. *Pathways and processes for CO_2 utilisation.*

methanol (CH_3OH), and methane, all of which are important platform chemicals for industry. Carbon monoxide, together with hydrogen (also called a syngas mixture) can be further converted to higher hydrocarbons via the Fischer-Tropsch process, a collection of reactions producing liquid hydrocarbons. Methanol can be used directly as a fuel, or be further converted by the methanol-to-olefin process. C_{2+} molecules (such as ethylene, ethanol, acetic acid, and propanol) are intrinsically more valuable than C_1 products, and they are harder to form due to the added difficulty of C–C bond formation between activated CO_2 intermediates.

Carbon dioxide can be catalytically reduced [...] (T)his can be a carbon-negative process, if the electricity comes from renewable sources

Carbon dioxide is a thermodynamically stable molecule; therefore, it needs a large energy input to convert it back to useful chemicals. The main technologies for CO_2 conversion are summarised in **Figure 2**, categorised by the energy input. Solar energy can be used by suitable light absorbers, such as natural plants, or artificial photocatalysts and photoelectrodes. Alternatively, CO_2 can be reacted with hydrogen in typically exothermic hydrogenation[3,4]. This usually yields C_1 products (CO, CH_4, CH_3OH), but bifunctional catalysts can also be used (*e.g.* to further convert CH_3OH to longer hydrocarbons *in situ*).

Here, we focus on one of the most promising routes – electrochemical CO_2 reduction[5]. Carbon dioxide can be catalytically reduced directly with metals, molecular complexes, or enzymes, concurrently with proton transfers (most commonly from H_2O). In principle, this can be a carbon-negative process, if the electricity comes from renewable sources.

Electrochemical CO_2 conversion – challenges to implementation

Lab-scale electrochemical CO_2 reduction has been widely studied since pioneering work on metal electrodes in the 1980s. One key limitation which has been overcome is the CO_2 supply to the electrode. In a normal batch-type cell (also called an H-cell, from the shape of two liquid compartments separated by a membrane), the limiting current density is on the scale of 12 mA/cm^2. This is estimated from the CO_2 solubility limit of 34 mM and a diffusion layer thickness of 100 µm, which is well below what is needed for industrial scale (> 200 mA/cm^2). An electrode structure called a gas-diffusion electrode can improve CO_2 transport by providing CO_2 as a gas stream through a porous support layer. Recent work in the area has demonstrated devices that operate at very high current densities which are > 1 A/cm^2, similar to commercial water electrolysers. Additionally, high Faradaic efficiency has been achieved (selectivity with regard to electrons), using a variety of catalysts from metals (Cu, Ag, Sn, *etc.*) and metal complexes (of Mn, Ni, Co, Fe, *etc*).

To bridge the gap between lab-scale and industrial-scale, technoeconomic analysis (TEA) has indicated that a significant part of the overall cost is from the processes upstream and downstream of the electrolyser itself[6]. In **Figure 3**, we show a typical process flow chart of CO_2 reduction, together with key parameters that we have identified as barriers to future implementation.

Process integration – CO_2 capture and source purity

Lab-scale CO_2 reduction typically uses high-purity CO_2 as the feedstock, because this allows the study of the catalyst and electrolyser performance without the complications from contaminants. However, real-world CO_2 waste streams from power generation and industrial processes (also called flue gas) will contain a mixture of other gases. Some contaminants such as H_2O or N_2 are benign, as they do not interfere directly with catalysis (although a large amount of diluent will lower the available CO_2 amount to some extent). Other contaminants (NO_x, SO_x, and especially O_2) are more detrimental, as they can poison the catalysts, or compete with CO_2 as the reducible material, leading to most of the input electrons being wasted. Purification of input CO_2, typically by amine-based capture and regeneration , adds significant cost to the overall process.

Industrial catalytic processes typically require durability on the 10,000-hour scale

One approach to circumvent this problem is to redesign the cell, for example with a perm-selective membrane, to allow less O_2 to reach the catalyst and therefore remove the need for pre-purification. Another approach is to directly reduce the capture media without using energy to regenerate gaseous CO_2. There are reports on direct reduction of carbonate or amine solutions, but the performances (current density and selectivity) are still below that of pure-CO_2 fed systems[7]. An additional problem is the degradation of the amine capture molecule, which could foul the system.

Process integration – downstream separation and regeneration

Up until the last few years, the CO_2 reduction community was mainly aiming to improve the Faradaic efficiency, decreasing the proportion of electrons lost to the competing hydrogen evolution reaction. This led to the use of highly alkaline catholytes (*e.g.* up to 10 M KOH), since hydrogen evolution is disfavoured at low proton concentrations. However, this was in essence replacing one problem with another, as the feed CO_2 reacts easily with hydroxides, forming bicarbonate and carbonate[8]. This CO_2 'lost' as carbonates cannot directly be used by the catalyst, and they need a large energy input to regenerate CO_2. An additional problem is that these undesired carbonates can cross-over through anion exchange membranes used in alkaline systems, contaminating the anode outlet stream and adding on separation costs.

To circumvent this problem, we demonstrated a selective CO_2 electrolyser configuration that uses bipolar membranes composed of cation and anion exchange layers[9]. With the cation exchange layer towards the cathode side, this prevents carbonate generation by presenting an acidic local environment. Other cell configurations have been proposed to tackle the problem of CO_2 loss[10]. For example, the electrode structure and local environment can be modified to suppress hydrogen evolution and to allow operation in acidic solutions. Another approach uses a two-stage setup, where the first stage is CO_2-to-CO in a solid oxide cell, and the second is CO-to-C_{2+} which can operate in alkaline solution since CO does not form the undesired carbonates.

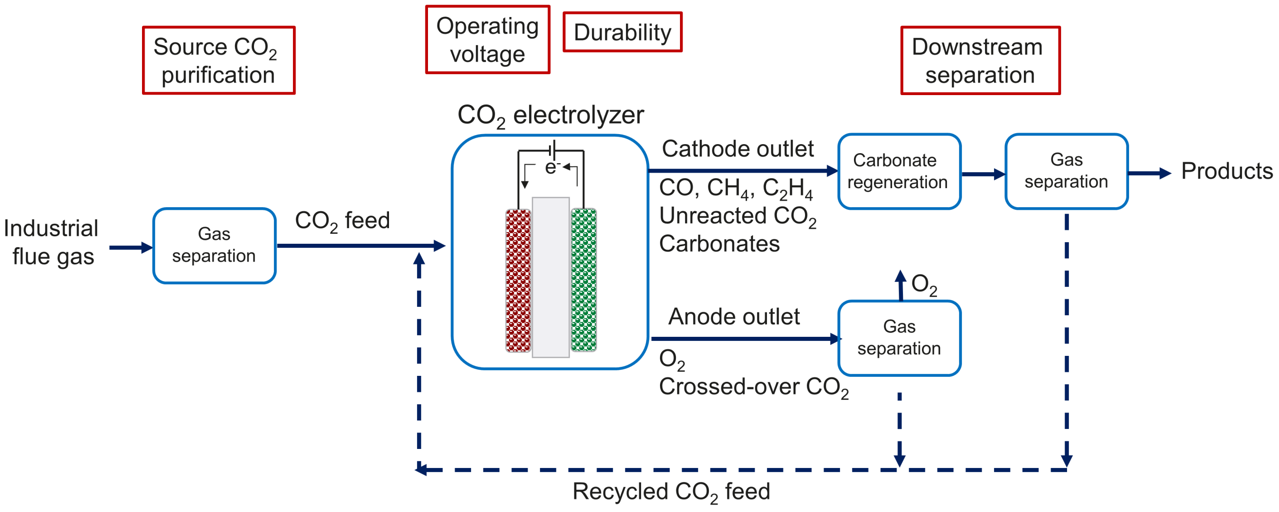


Figure 3. *A schematic overview of the electrochemical CO_2 reduction process, with key parameters highlighted in red.*

Durability

Industrial catalytic processes typically require durability on the 10,000-hour scale, since reactor downtime and catalyst replacement would significantly increase costs. However, typical laboratory experiments are still conducted on the 10-100s of hours scale. The longest demonstration showed a device under continuous operation for 3800 hours (> 5 months)[11].

A CO_2 electrolyser is a complex device with numerous possible failure modes. First, the catalyst can aggregate or degrade, akin to a typical catalytic reactor. This is especially problematic if the performance of the catalyst relies on a certain facet (for metal catalysts) or on the dispersed nature (of molecular complexes or single-atom materials). Second, the ion-conducting membrane separating the cathodes and anodes can also degrade.

Finally, the electrode structure itself is prone to flooding and blockage, since its complex structure is necessitated by concurrently supplying electrons, protons, and CO_2 to the catalyst. The structure of a gas-diffusion electrode is a porous and hydrophobic conductive support, upon which a catalyst layer is typically deposited. Ideally, the porous support provides gas channels for fast transport of CO_2 to the catalyst, which is minimally wetted such that there is enough H_2O to provide protons, but not present a large impediment to CO_2 transport[12]. However, under realistic operating conditions, H_2O is generated as a by-product, as well as transported across from the anode compartment. If the pores in the support are flooded with excess H_2O, the CO_2 supply to the catalyst will be lower, thus limiting the achievable current. Therefore, careful water management and monitoring is necessary.

Outlook

Electrochemical CO_2 reduction is on the cusp of becoming an industrial-scale technology for converting waste CO_2 back into valuable chemicals. We consider it to be at TRL (Technology Readiness Level) ~3-4 with a small number of systems reaching TRL 5, as CO_2 electrolysers have been clearly demonstrated at the lab-scale, while trying to move closer to industry-relevant conditions. There are multiple start-up companies in this field, usually based on the expertise of research groups in CO_2 electrochemistry.

There are clear examples of electrochemical processes that have been successfully translated to a fully industrial scale. The chlor-alkali process (the electrolysis of NaCl solution to generate NaOH, H_2, and Cl_2) was used to generate more than 9 million tonnes of Cl_2 in Europe in 2021. Water electrolysers and fuel cells have also been commercialised, and the modular nature of electrochemical cells and stacks help to simplify scaling-up once a pilot-size electrolyser is developed. With renewable electricity becoming more prevalent, electrochemical CO_2 reduction can become a major pathway to achieve a circular carbon economy.

Acknowledgements

This work has been supported by UKRI-EPSRC funding to the Interdisciplinary Centre for the Circular Chemical Economy (EP/V011863/2).

References

1. T. Keijer, V. Bakker & J.C. Slootweg, Circular chemistry to enable a circular economy. *Nature Chemistry,* 2019**, 11** (3), 190-195. https://doi.org/10.1038/s41557-019-0226-9
2. H. Ritchie, M. Roser & P. Rosado, CO_2 and Greenhouse Gas Emissions. *Our World in Data,* 2020.
3. A. Álvarez, A. Bansode, A. Urakawa, A.V. Bavykina, T.A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO_2 Hydrogenation Processes. *Chemical Reviews,* 2017**, 117** (14), 9804-9838. https://doi.org/10.1021/acs.chemrev.6b00816
4. R.-P. Ye, J. Ding, W. Gong, M.D. Argyle, Q. Zhong, Y. Wang, C.K. Russell, Z. Xu, A.G. Russell, Q. Li, M. Fan, Y.-G. Yao, CO_2 hydrogenation to high-value products via heterogeneous catalysis. *Nature Communications,* 2019**, 10** (1), 5698. https://doi.org/10.1038/s41467-019-13638-9
5. M.G. Kibria, J.P. Edwards, C.M. Gabardo, C.-T. Dinh, A. Seifitokaldani, D. Sinton, E.H. Sargent, Electrochemical CO_2 Reduction into Chemical Feedstocks: From Mechanistic Electrocatalysis Models to System Design. *Advanced Materials,* 2019, **31** (31), 1807166. https://doi.org/10.1002/adma.201807166
6. A. Somoza-Tornos, O.J. Guerra, A.M. Crow, W.A. Smith, B.-M. Hodge, Process modeling, techno-economic assessment, and life cycle assessment of the electrochemical reduction of CO_2: a review. *iScience,* 2021**, 24** (7), 102813. https://doi.org/10.1016/j.isci.2021.102813
7. S.E. Jerng & B.M. Gallant, Electrochemical reduction of CO_2 in the captured state using aqueous or nonaqueous amines. *iScience,* 2022**, 25** (7), 104558. https://doi.org/10.1016/j.isci.2022.104558
8. J.A. Rabinowitz & M.W. Kanan, The future of low-temperature carbon dioxide electrolysis depends on solving one basic problem. *Nature Communications,* 2020, **11** (1), 5231. https://doi.org/10.1038/s41467-020-19135-8
9. B. Siritanaratkul, M. Forster, F. Greenwell, P.K. Sharma, E.H. Yu, A.J. Cowan, Zero-gap bipolar membrane electrolyzer for carbon dioxide reduction using acid-tolerant molecular electrocatalysts. *Journal of the American Chemical Society,* 2022**, 144** (17), 7551-7556. https://doi.org/10.1021/jacs.1c13024
10. A. Ozden, F.P. García de Arquer, J.E. Huang, J. Wicks, J. Sisler, R.K. Miao, C.P. O'Brien, G. Lee, X. Wang, A.H. Ip, E.H. Sargent, D. Sinton, Carbon-efficient carbon dioxide electrolysers. *Nature Sustainability,* 2022**, 5** (7), 563-573. https://doi.org/10.1038/s41893-022-00879.-8
11. Z. Liu, H. Yang, R. Kutz, & R.I. Masel, CO_2 Electrolysis to CO and O_2 at high selectivity, stability and efficiency using sustainion membranes. *Journal of The Electrochemical Society,* 2018 **165** (15) J3371-J3377. https://doi.org/10.1149/2.0501815jes
12. N.T. Nesbitt, T. Burdyny, H. Simonson, D. Salvatore, D. Bohra, R. Kas, W.A. Smith, Liquid–solid boundaries dominate activity of CO_2 reduction on gas-diffusion electrodes. *ACS Catalysis,* 2020**, 10** (23), 14093-14106. https://doi.org/10.1021/acscatal.0c03319

Article

Transforming CO_2 into construction products

Colin D. Hills and Nimisha Tripathi
(University of Greenwich, c.d.hills@gre.ac.uk, n.tripathi@gre.ac.uk)

The UK government's recent decision to invest £20 billion in a carbon capture, utilisation, and storage (CCUS) infrastructure fund, is a significant boost for using anthropogenic CO_2 gas to manufacture consumer products as diverse as jet fuel or building materials. The UK has been leading in the latter area since 2012, when the world's first full-scale facility for manufacturing carbonated construction aggregates was established in East Anglia. Neither the potential to transform gigatonnes of anthropogenic CO_2 into limestone, nor the similarities between mineralisation technology and natural Earth processes are fully appreciated.

The use of man-made cementitious mortars extends back 10,000 years[1]. Around 25 BC, Vitruvius, a Roman architect and engineer, was recommending combinations of volcanic ash and lime mortars for construction projects; some are still in service today[2,3]. In part, the longevity of these Roman mortars is the result of the reaction of carbon dioxide gas in the atmosphere with quicklime to form calcium carbonate (**Eq.1**, below). The resulting carbonated mortar is more thermodynamically stable, durable, and relatively forgiving of structural movement.

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad \textbf{Eq.1}$$

What is not fully recognised are the parallels between manmade carbonated materials and those made by natural processes. In nature, CO_2 is mineralised in the weathering of rock, or by chemical and biologically-mitigated reactions in the oceans or in soil.

These reactions result in carbonate being effectively stored in the geosphere over geological time scales - harmful gas is

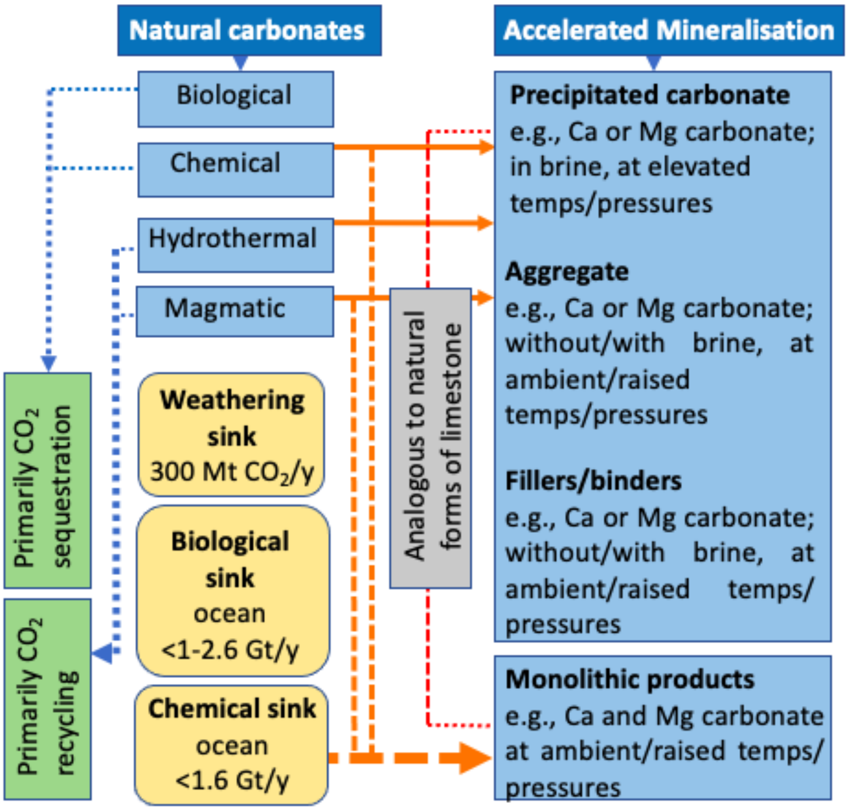


Figure 1. *Comparison of natural and assisted carbonation for selected EU waste streams [Reproduced from [18]].*

permanently 'locked up' and thus, cannot adversely impact the climate and ecosystems.

Our planet is good at partitioning carbon and the billions of Gts of carbon stored in the geosphere represent about 99% of the Earth's total reserves. According to the Deep Carbon Observatory, these carbon reserves are in the order of 1.85 x 10^{18} tonnes[4], with most being carbonates in sedimentary rocks – of which limestone accounts for about 4.0 x 10^{17} tonnes[5]. The feedback time for the amelioration of anthropogenic CO_2 is in the order of hundreds of millennia, thus, for us to moderate our climate, industrialisation of carbon transformation is required. CCUS has potential to make a difference in the shorter-term by processing anthropogenic carbon into manufactured products. As carbon utilisation is complementary to carbon storage, both strategies are needed to meet the UK's emission reduction goals, reflected in recent investment by the UK Government[6,7].

The billions of Gts of carbon stored in the geosphere represent ~99% of the Earth's total 'reserves'

CO_2 gas can be used as a feedstock to make a diverse range of products, from kerosene and polymers to fertiliser and construction aggregates. The world market of the latter is in the region of 50 Gt each year[8], well placed to receive carbonated aggregates made from anthropogenic CO_2.

Managed carbonation

Chemical processes that can transform CO_2 can involve the use of high temperatures and pressures, and chemical reagents. To keep associated emissions to a minimum, energy intensive processes utilising fossil fuels should be avoided wherever possible.

Our work is focused on using ambient temperatures and pressures during processing[9]. The resultant calcium carbonate-based products have high positive environmental carbon offsets via the direct removal and permanent capture of flue-gas derived CO_2. Indirect offsets include reduced use of virgin materials and the avoidance of quarrying, crushing, and transportation.

Many industrial alkaline waste streams are excellent substrates to mineralise CO_2 upon allowing wastes to also be risk managed and diverted from landfill.

The estimates of suitable waste streams worldwide for use as mineralisation vary from 1-4 Gt/yr. These process wastes tend to be closely associated with point-source CO_2 emissions, creating an opportunity to combine solid and gaseous emissions at one site. In Europe, there is potential to sequester ca. 7.8 Mt/yr of CO_2 in 79 Mt of alkaline residues from five different waste streams: municipal solid waste incinerator; biomass; paper and oil shale ashes; steel slag; and construction and demolition waste. Waste arisings such as these are carefully documented[10].

Kinetic constraints upon carbonation have been summarised by the IPCC[11] who concluded that high-grade energy is required to drive the mineral carbonation process and that (without refining), direct carbonation with flue gas must include raised pressures. This is not strictly true as the direct use of flue gas is achieved under ambient conditions[12,13].

Managed carbonation pathways

It is useful to describe managed carbonation as falling into three applications based on the amount of water use in the reaction process:

(i) Wet carbonation involves a water/solids ratio above 0.4 w/w (total wt.). This route is normally applied to mineral suspensions in aqueous solution in which CO_2 is dissolved in a batch reactor under mild conditions, but can involve elevated temperatures and pressures. The products tend to be relatively pure, fine-grained precipitated calcium carbonate[14].

(ii) Semi-dry carbonation (or direct carbonation) using water/solid ratios below < 0.4 w/w, typically < 0.3 w/w (total weight). This reaction environment enables the formation of a thin film of moisture on the surface of minerals to facilitate rapid dissolution and ionisation of CO_2, enabling carbonation to proceed quickly. Monolithic products may be manufactured.

(iii) Assisted carbonation, where temperatures and pressures are significantly raised above ambient conditions, possibly exceeding 250°C and 2 MPa. Processing may involve digestion, use of proprietary solvents/chemicals (which, in themselves may require energy intensive forms of preparation/synthesis), or the application of supercritical CO_2[15]. Diverse products may be manufactured.

Figure 1 summarises the relationship between natural and managed carbonation, and potential net gain via CO_2 sequestration (direct and indicative indirect offsets[16,17,18]).

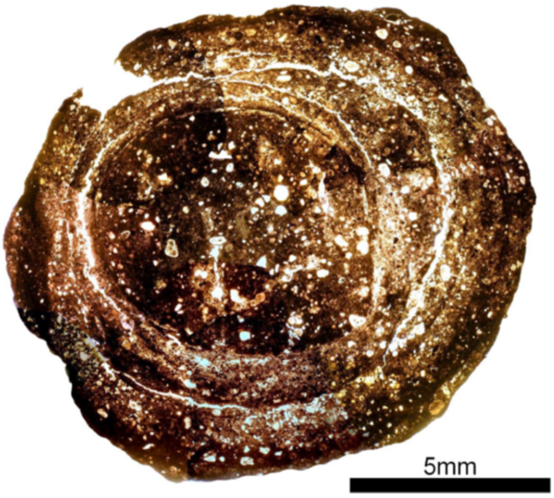


Figure 2. *Transmitted light micrograph of a concentric structure within a manufactured carbonated aggregate.*

Our interest is the semi-dry carbonation of alkaline solid industrial process residues, containing mineral components that readily react with CO_2 gas. As outlined in (ii) above, the products are analogous to natural carbonates formed at or near the Earth's surface, where temperatures and pressures are generally low, and the prevalent chemical environment tends to be alkaline/saline. The products of managed mineralisation include precipitated carbonates, light-weight aggregates, fillers/binders, or shaped monoliths.

Notably, the transmitted light micrograph shown in **Figure 2** is of a laboratory-manufactured carbonated aggregate comprising an air pollution control residue. The concentric layered structure of the aggregate is built around a central core and is analogous in structure to that displayed by pisoliths formed in terrestrial, lacustrine, and marine environments[19,20].

The natural formation of limestone over geological time scales and the production of carbonated products via mineralisation are demonstrably analogous, but the latter is achieved in minutes, whereas the former are made over extended timescales by *natural* processes including chemical, biological, and magmatic.

Conclusion

Directly combining solid and gaseous wastes from single or multiple emitters is circular. Technology established in the UK can be extended to different industrial solid waste feedstock, and result in manufactured carbonated construction products for a variety of applications. As indicated by GCI[21], there is potential to utilise 3-6 Gt of anthropogenic CO_2 in construction materials and generate annual revenues of $1 trillion each year.

References

1. D. Carran, J. Hughes, A. Leslie, C. Kennedy, A short history of the use of lime as a building material beyond Europe and North America. *International Journal of Architectural Heritage*, 2012 **6**(2), 117–146. https://doi.org/10.1080/15583058.2010.511694
2. Limebase. http://www.limebase.co.uk/guides/the-history-of-lime-mortar/#:~:text=The%20Romans%20developed%20a%20hydraulic,to%20pozzolan%20for%20underwater%20works [*Accessed April 2023].*
3. L. M. Seymour, J. Maragh, P. Sabatini, M. Di Tommaso, J. C. Weaver, A. Masic, Hot mixing: Mechanistic insights into the durability of ancient Roman concrete. *Science Advances*, 2023 **9**(1), eadd1602. https://doi.org/10.1126/sciadv.add1602
4. Deep Carbon Observatory. Deep carbon observatory: A decade of discovery. Deep Carbon Observatory Secretariat. 2019 https://doi.org/10.17863/CAM.44064
5. L. R. Kump, J. F. Kasting, & R. G. Crane, *The Earth System,* Pearson pubs, London, 2004
6. The ten point plan for a green Industrial Revolution, http://www.gov.uk/government/publications/the-ten-point-plan-for-a-green-industrial-revolution/title (*Accessed December 2020).*
7. *Upstreamonline*, http://www.upstreamonline.com/energy-transition/uk-earmarks-20-billion-for-carbon-capture-and-storage-funding/2-1-1420257 (*Accessed: April 2023).*
8. United Nations. Sand and sustainability: 10 strategic recommendations to avert a crisis. Global resource information database. *EP*. 2022. https://unepgrid.ch/storage/app/media/Publications/2022sandandsustainabilityreportfinal.pdf
9. P. J. Gunning, C. D. Hills, and P. J. Carey, Production of lightweight aggregate from industrial waste and carbon dioxide. *Waste Management*, 2009, **29**(10), 2722–2728. https://doi.org/10.1016/j.wasman.2009.05.021
10. Eurostat, https://ec.europa.eu/eurostat/en/web/products-key-figures/w/ks-ei-23-001(*Accessed July 2023)*
11. IPCC. IPCC special report on carbon dioxide capture and storage. *Prepared by working group* B. Metz, O. Davidson, H. C. de Coninck, M. Loos & L. A. Meyer (Eds.), *III of the Intergovernmental Panel on Climate Change*, 2005, p. 442. Cambridge University Press.
12. J. H. Kim, and W. T. Kwon, Semi-dry carbonation process using fly ash from solid refused fuel power Plant. *Sustainability*, 2019, **11**(3), 908. https://doi.org/10.3390/su11030908
13. *Carbon*, *8*, http://www.carbon8.co.uk (*Accessed April 2023).*
14. H. Ostovari, A. Sternberg, and A. Bardow, Rock 'n' use of CO_2: carbon footprint of carbon capture and utilization by mineralization *Sustainable Energy and Fuels*, 2020, **4**(9), 4482–4496. https://doi.org/10.1039/D0SE00190B
15. S. Chakraborty, and B. W. Jo, B. W. In *Carbon Dioxide Sequestration in Cementitious Construction Materials*, ed. F. Pacheco-Torgal, Caijun Shi & A. Palomo Sanchez , Woodhead Publishing, Cambridge, 2018, pp. 39-64 https://doi.org/10.1016/B978-0-08-102444-7.00003-4
16. S. A. Rackley, *Carbon Capture and Storage* (2nd ed), Butterworth-Heinemann, Oxford, 2017. https://doi.org/10.1016/C2009-0-19306-6
17. L. Ji, and H. Yuin *Carbon Dioxide Sequestration in Cementitious Construction Materials*, ed. F. Pacheco-Torgal, Caijun Shi & A. Palomo Sanchez, Woodhead Publishing, Cambridge, 2018, pp. 13–37. https://doi.org/10.1016/B978-0-08-102444-7.00002-2
18. C. D. Hills, N. Tripathi, and P. J. Carey, Managed pathways for CO_2 mineralisation: analogy with nature and potential contribution to CCUS-led reduction targets. *Faraday Discussions*, 2021, **230**, 152–171. https://doi.org/10.1039/d0fd00142b
19. D. F. Lascelles, The origin of terrestrial pisoliths and pisolitic iron ore deposits: Raindrops and sheetwash in a semi-arid environment. *Sedimentary Geology*, 2021, **341**, 232–244. https://doi.org/10.1016/j.sedgeo.2016.04.015 0037-0738.
20. D. K. Richter, In *Coated Grains*, ed. T. M. Peryt, Springer, New York, 1983.https://doi.org/10.1007/978-3-642-68869-0_7
21. GCI, Global CO_2 Initiative, http://www.globalco2initiative.org [Retrieved April 2023].

ECG Environmental Brief No. 37 **ECGEB No. 37**

Vitrification: Using thermal methods to increase long-term stability of geological disposal of radioactive waste

Lauren Harford (University of Reading, l.harford@student.reading.ac.uk)

Nuclear power provision has grown over past decades to keep up with consumer demand for a renewable and clean energy future. To generate this electricity, nuclear fission of uranium-235 atoms causes a chain reaction resulting in vast amounts of heat/radiation energy being released. These reactions produce unwanted radioactive materials (*e.g*. spent fuel rods) or waste, which is extremely harmful to humans[1], animals and the environment.

Radioactive Waste Disposal

Between 1949-1983[2], many radioactive waste materials, especially those that are low-level (LLW) and intermediate-level (ILW), such as protective clothing, were disposed of in the oceans[3]. How these are now disposed of can be seen in **Figure 1**. Within the UK, the most preferred way of radioactive waste disposal is using deep geological disposal facilities (GDF). An alternative disposal in space[4] could provide permanent safety and solve the problem of demand but is dependent on complex technology advances.

To achieve GDF, suitable locations for long-term stability must be found away from humans, animals and the environment. This is primarily for the safety of high-level waste (HLW) (*e.g.* spent fuel rods); with the last Nuclear Decommissioning Authority (NDA) report stating ~3,200 tonnes of HLW were generated in 2019[5]. These are currently stored in overground spent fuel tanks as interim storage[3], but plans are being made in the UK for deep GDF (**Figure 1**). The idea is that GDF will ensure the long-term stability of radioactive waste disposal, and this can be achieved through thermal methods.

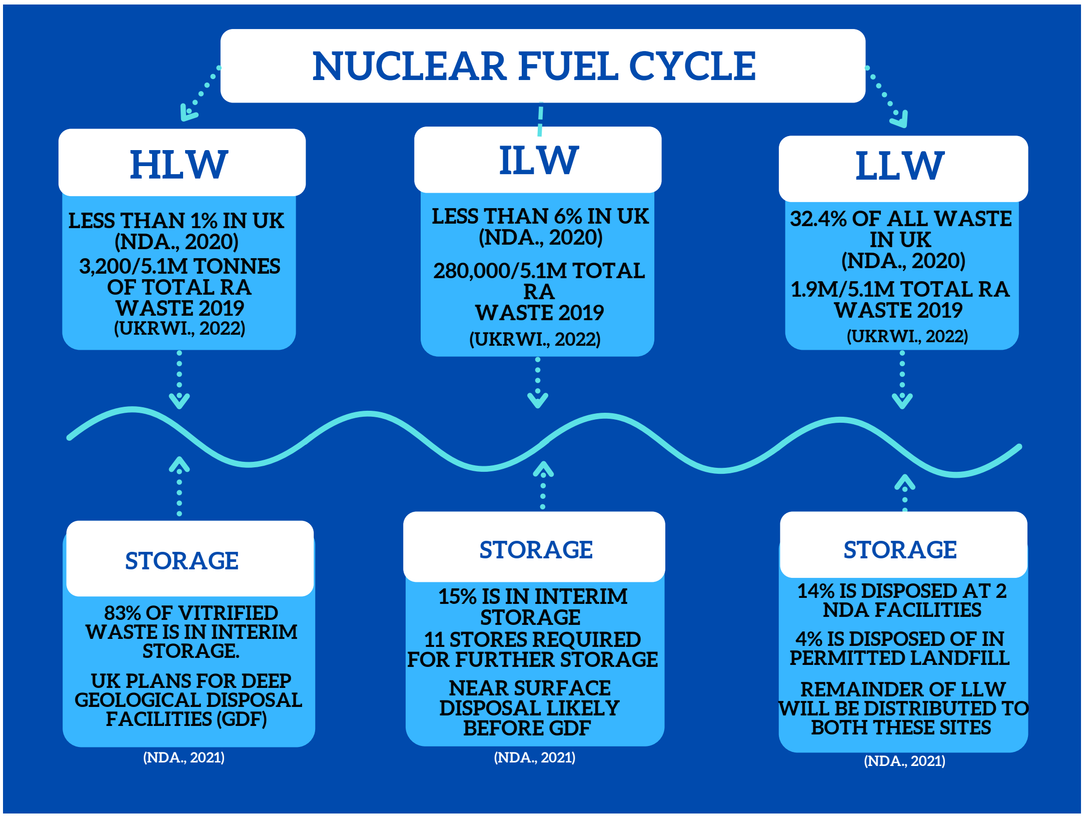


Figure 1. *Flow chart showing the types of radioactive waste generated and how they are stored/disposed of within the UK.*

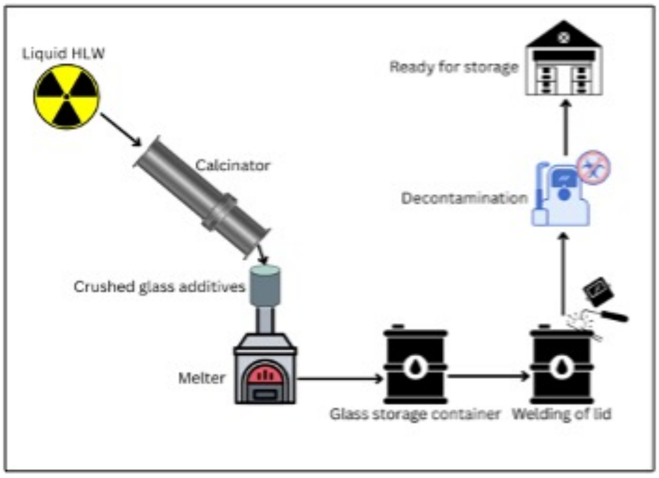


Figure 2. Ex situ *vitrification (ESV) process converting radioactive waste to a storage-suitable material.*

Thermal Methods

Thermal treatment of radioactive waste involves any technology using high temperatures to reduce the total mass of the radioactive waste, eliminate hazardous organic substances, and stabilise harmful components – these tend to be leach-resistant *i.e.* glass or ceramic. Thermal processing decreases mass, whilst also preventing any leaching from other water streams onto the waste. Processes include vitrification, incineration, distillation, and pyrolysis to separate toxic components from liquid solutions. This enables mass reduction of volume through combustion within an advanced filtering system[6].

~3,200 tonnes of HLW were generated in 2019. Vitrification process shows a more efficient disposal route.

Vitrification

Vitrification is the most important method within waste management as it increases the long-term stability of geological disposal. It describes the conversion of a material into a glassy matrix whereupon radioactive waste may be stabilised before it is stored underground. For deep geological storage of radioactive waste, *ex situ* vitrification (ESV) is necessary to produce a storage-suitable product. It uses a melting furnace where the liquid waste is heated through a calcinator (**Figure 2**), which is then cooled after excretion. Calcinated materials with crushed glass are added to the melter to bond the radioactive waste to the glass, thus immobilising hazardous waste for thousands of years[6].

This process has been successful in France, with the Marcoule Plant, and in the UK at the Sellafield Plant, following a £240 million investment and research confirming reduced volume, improved safety, and long-term stability of vitrified radioactive waste material[7].

Conclusion

Using vitrification as the thermal method of HLW disposal has been shown to be safe and efficient, with the possibility of retaining radionuclides for hundreds of thousands to possibly millions of years.

References

1. K.R Rao, Radioactive waste: The problem and its management. *Current Science*, 2001, **81**(12),1534-1546.
2. K.L. Sjoeblom & G. Linsley, Sea disposal of radioactive wastes: The London Convention 1972. *IAEA Bulletin*, 1994 **36**(2), 12-16.
3. J. Rieuwerts, *The Elements of Environmental Pollution*, Routledge, London, 2017.
4. J. Coopersmith, Nuclear Waste Disposal in Space: BEP's Best Hope? *AIP Conference Proceedings*, 2006, **830**, (1), 600-604
5. GOV (2021) The Nuclear Decommissioning Authority Mission Progress Report 2021, https://www.gov.uk/government/publications/nuclear-decommissioning-authority-mission-progress-report-2021, (Accessed: November 22, 2022).
6. L. Fuks, I. Herdzik-Koniecko, K. Kiegiel, A. Miskiewicz, G. Zakrzewska-Koltuniewicz, Methods of thermal treatment of radioactive waste. *Energies*, 2022, **15**(1), p.375. https://doi.org/10.3390/en15010375
7. Innovative Technology for safe and cost-efficient radioactive waste management, https://www.sheffield.ac.uk/materials/research/our-research-impact/innovative-technology-safe-and-cost-efficient-radioactive-waste-management, (Accessed November 2022)

Table 1. *Advantages and disadvantages of* ex situ *vitrification .*
Data from Reference [6]*.*

Advantages	Disadvantages
High volume reduction of up to 90%	High initial investment/ operating costs
Efficient and fast acting	Appropriate geological disposal location is needed for approval first which is difficult to locate
Increases long-term stability	Volatile radionuclides in ESV system may cause danger to staff and environment in process.

The sources and impacts of polystyrene nanoplastics (PSNPs)

Yifan Du (University of Reading, yifan.du@student.reading.ac.uk)

Polystyrene plastic products are widely used in everyday life and, through diverse processes, they may be broken down into nanoplastics with particles less than 1000 nm in diameter. Polystyrene nanoplastics (PSNPs) are difficult to degrade and can accumulate in the environment for many years, causing serious pollution to ecosystems and their organisms. This Environmental Brief summarises their main sources and major impacts.

Due to their high-quality properties, plastics have become an integral part of our lives and can be found in almost every field. The global annual production of plastics soared from 1.5 million tonnes in 1950 to just under 370 million tonnes in 2019[1]. However, most plastic wastes are difficult to recycle; more than 8 million tonnes of them enter the oceans globally each year[2] and spread by water and wind, causing serious pollution to the natural environment, including the atmosphere, water bodies and soil. In addition, the debris can easily enter animals and humans through air, food, and drinking water, posing a potential threat to the health of living organisms[3,4].

In 2019, the global production capacity of polystyrene was 15.6 million metric tonnes[1]. As one of the most widely used plastics, it is also one of the most important sources of nano-plastic wastes. Research conducted by Kik *et al.* (2020) has shown that PSNPs can penetrate into organisms through multiple pathways, including the skin, respiratory and digestive tracts, and can be enriched through the food chain[2]. Control of the sources and effects of PSNPs is an urgent priority.

Sources

Polystyrene (PS) has been widely used in food, toy and industrial packaging, building insulation, and medical equipment industries due to its abundant raw material sources, simple polymerisation process and properties (light, inexpensive, transparent, insulating, corrosion resistant and easy colouring)[3,5]. PS particles less than 1000 nm in diameter are categorised as polystyrene nanoplastics (PSNPs)[2,4]. Depending on the process from which they originate, they can be mainly divided into two groups: primary and secondary PSNPs. The former are derived from the release of PSNPs added directly to cosmetics, bioimaging and sensing, nano-pharmaceuticals and electronics and waterproof coatings[1]. They also serve as precursors for the synthesis of other polymer products, which escape during processing[3]. At present, most studies on the toxicity of PSNPs have focused on primary NPs.

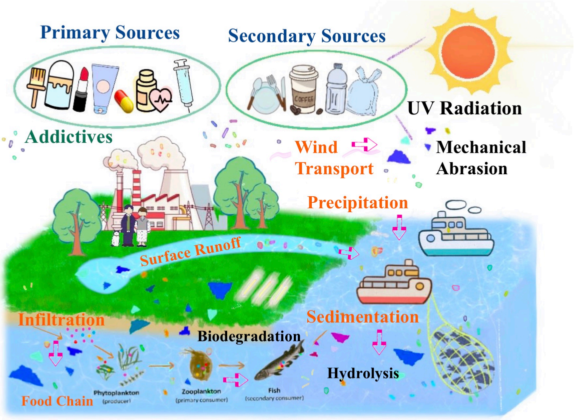


Figure 1. *Sources and transport of PSNPs.*

In contrast, after entering the environment, polystyrene plastic products break down into secondary microplastics (MPs) through continuous external processes like mechanical abrasion, hydrolysis, and biodegradation[4], and are further decomposed into plastic particles less than 1000 nm in diameter (secondary PSNPs). Prolonged sunlight exposure can lead to photodegradation of plastics, as the ultraviolet (UV) radiation in sunlight can break the C-H bonds in polystyrene molecules[6]. With the loss of integrity, these plastics are more likely to be broken due to wear, weathering and turbulence, which can lead to the gradual degradation of fragments into nanoscale particles[4,6].

Polystyrene nanoplastics (PSNPs) can reach anywhere in the world by entering the atmosphere, hydrosphere, soil and even the biosphere through water and atmospheric cycles[1,4]. They can be found in drinking water, wastewater, sludge, compost and atmospheric sediments[2,5]. **Figure 1** depicts the main sources and transport processes of PSNPs. PSNPs in aquatic bodies mainly come from terrestrial inputs, fishing activities and ship discharges [6], and their mobility is largely dependent on their suspension capacity and particle size[6,7].

Sewage treatment plants are considered an important hub for plastic particles between human society and the natural environment[5]. In the atmosphere, PSNPs mainly originate from synthetic fibres in construction materials, waste incineration and landfills[8], and are transported by wind and natural deposition. Agricultural film residues, the use of sludge and organic fertilisers, surface water irrigation, atmospheric deposition, landfill and waste disposal are main sources of soil PSNPs [3]. In addition, environmental

PSNPs can enter food and drinking water in various ways, to then spread and accumulate through the food chain and food web, causing pollution and hazards [4].

Impacts

The toxicity of PSNPs is higher than that of ordinary plastics. Due to their size and high penetrating power, PSNPs can enter the organism through various channels (air, food, water, and skin) and accumulate in tissues[5]. PSNPs can pass through the food chain to consumers, causing deleterious effects[2]. PSNPs have a large specific surface area and may adsorb pollutants from the environment (*e.g.* heavy metals, polycyclic aromatic hydrocarbons, and antibiotics), causing combined toxicity[1,4]. Furthermore, PSNPs can act as carriers for some microorganisms, spreading globally by wind and hydrological processes such as ocean currents[3], leading to species invasion and spread of resistant bacteria and resistance genes[6].

Recent research by Wu *et al.* (2020) found that PSNPs can attach to the seed coat of soybean, reducing the rate of water and nutrient uptake thereby inhibiting seed vigour[8]. Experiments on lettuce showed that the toxicity of PSNPs is higher through foliar contact than root contact, probably due to the restriction of stomata that affects photosynthesis and respiration[3]. For animals, PSNPs can pass through the circulatory system, affecting the liver, kidneys and pancreas. They can even cross the blood-brain barrier into the brain, inducing oxidative stress, inflammatory responses, neurotoxicity, metabolic disorders and behavioural disturbances in tissues[1,2]. Studies in mice found exposure to high concentrations of PSNPs (200 mg/L for 48 h) reduced the viability of neuronal cells[3], 10 mg/L for 20 days developed tissue structural changes, lipid digestion problems, and blood frame damage; while aggregation was seen in the spleen, intestine, lungs, kidneys and brain[9].

Inhaled PSNPs tend to remain in the human respiratory system and gastrointestinal tract, which may cause DNA damage and contribute to cancer[2,5].

Conclusion

PSNPs are diverse in origin and widespread in various environmental media worldwide (**Figure 1**). Studies have shown that PSNPs are toxic to organisms and pose a threat to human health through the food web, inhalation and dermal exposure (**Figure 2**). However, animal studies are relatively narrow in subject, and the short duration and high concentrations of exposure make it hard to provide evidence of the risks of long-term daily exposure. In addition, the effects of PSNPs on humans are mainly based on human-derived cells and animal models, and there are no uniform criteria for determining their toxic effects. What is more, the research methods are relatively homogeneous.

In the future, it is imperative to develop new approaches to explore the effects of nano-plastic pollution and to further control plastic pollution and reduce its adverse effects through policy introduction, technological innovation and people's implementation.

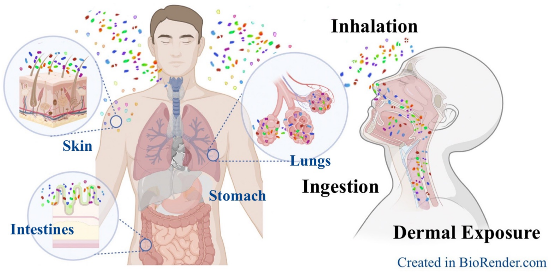


Figure 2. *Main pathways of human exposure to PSNPs.*

References

1. J. Zhang & D Li, Review on the occurrence, analysis methods, toxicity and health effects of nano-plastics in the environment, *Environmental Chemistry*, 2021, **40**(1), 28-40. http://dx.doi.org/10.7524/j.issn.0254-6108.2020062003
2. K. Kik, B. Bukowska, & P. Sicińska, Polystyrene nanoparticles: Sources, occurrence in the environment, distribution in tissues, accumulation and toxicity to various organisms, *Environmental Pollution*, 2020, **262**, 114297. https://doi.org/10.1016/j.envpol.2020.114297
3. C. Gupta, S. Kaushik, S. Himanshu *et al.*, Bioaccumulation and toxicity of PSNPs on marine and terrestrial organisms with possible remediation strategies, *Environmental Advances*, 2022, **8**, 100227. https://doi.org/10.1016/j.envadv.2022.100227
4. D. Huang, J. Tao, M. Cheng, *et al.* , Micro/nano-plastics in the environment: Macroscopic transport and effects on creatures, *Journal of Hazardous Materials*, 2021, **407**, 124399. https://doi.org/10.1016/j.jhazmat.2020.124399
5. R. Lehner, C. Weder, A. Petri-Fink & B. Rothen-Rutishauser, Emergence of Polystyrene Nanoplastic in the Environment and Possible Impact on Human Health, *Environmental Science and Technology*, 2020, **53**(4), 1748-1765. https://doi.org/10.1021/acs.est.8b05512
6. M. Piccardo, M. Renzi, & A. Terlizzi, Nanoplastics in the oceans: Theory, experimental evidence and real world, *Marine Pollution Bulletin*, 2020, **157**, 111317. https://doi.org/10.1016/j.marpolbul.2020.111317
7. M.T. Ekvall, M. Lundqvist, E. Kelpsiene, E. Sileikis, S.B. Gunnarsson, T. Cedevall, Nanoplastics formed during the mechanical breakdown of daily-use polystyrene products, *Nanoscale Advances*, 2019, **1**(3), 1055-1061. https://doi.org/10.1039/C8NA00210J
8. J. Wu, T. Yang, J. Lian et al., Effect of polystyrene nanoplastics (PSNPs) on seeds germination and seedling growth of soybean (Glycine max.), *Acta Scientiae Circumstantiae*, 2020, **40**, 4581–4589. (In Chinese). Cited in X. Mao, Y. Xu, Z. Cheng et al., The impact of microplastic pollution on ecological environment: a review, *Frontiers in Bioscience (Landmark Edition)*, 2022, **27**(2), 046. http://doi.org/10.31083/j.fbl2702046
9. D. Xu, Y. Ma, X. Han, Y. Chen, Systematic toxicity evaluation of PSNPs on mice, *Journal of Hazardous Materials*, 2021, **417**, 126092. https://doi.org/10.1016/j.jhazmat.2021.126092