RSC INTEREST GROUP
ENVIRONMENTAL CHEMISTRY

July 2021

Environmental Chemistry Group Bulletin

25 years of *Bulletins*, 200 committee meetings.

Articles. Clare Thorpe studies glassy material longevity for safe disposal of vitrified nuclear wastes. Zhugen Yang announces a paper-origami device for selective, cost-effective sewage tests. David Owen reflects on changes in environmental chemistry and legislation. Two #RSCPoster Twitter Conference participants showcase their work.

Upcoming meetings. We announce three in-person meetings, including our Distinguished Guest Lecture on electronic waste and disposable attitude.

Environmental Briefs. Caroline Thomas examines changes to atmospheric pollution and Rebecca Kent single use plastic during the pandemic. Michael Eze discusses microbially-enhanced bioremediation and Rachel Schwartz-Narbonne bacteriohopanepolyol lipids.

Also in this issue. Tomás Sherwen leads us to atmospheric research. Laura Alcock reviews advanced oxidation technology, and Rowena Fletcher-Wood reviews presentation training. Our colour changing chemistry Outreach Activity is included.

Foreword from the Chair

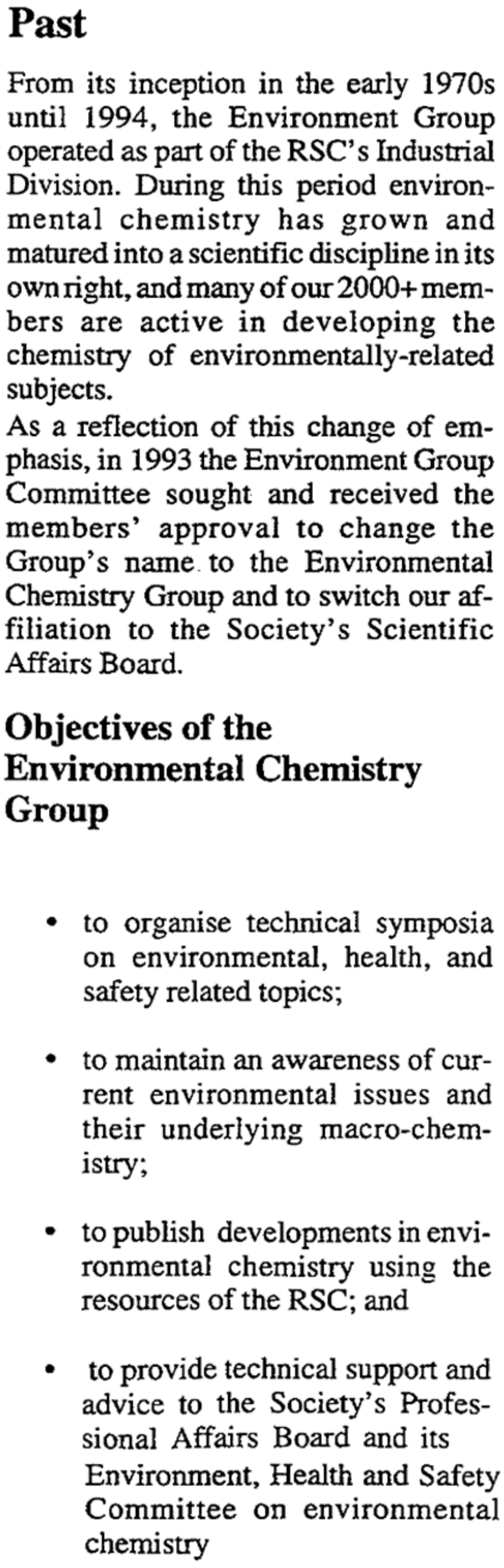
This year, the ECG celebrated its 200th committee meeting, and 25 years of *Bulletins* – originally known as the *Environmental Chemistry Group Newsletter*. This landmark comes at an interesting time, as we pull back from most in-person meetings during the COVID-19 pandemic and reflect on the role, purpose, and aims of the group.

Across 2020 and 2021, the group has seen a movement towards desktop conferences and meetings, hosting the highly successful #EnvChem2020, where we attracted a global audience and learnt valuable lessons in the facilitation of online events (reported in our January 2021 *Bulletin*). Recently, we sponsored the #RSCPoster Twitter Conference, encouraging scientific discussion without borders. All of our committee meetings have been online, and we are considering a mixture of both in-person and online meetings for the future, enabling greater accessibility (and so a greater diversity of committee members), without the loss of valuable face-to-face interactions and networking. Whilst we look forward to the return to physical meetings, we are exploring the possibilities for streaming or recording meetings to enable wider access.

As we reflect on these changes, we also consider those the environmental chemistry group has seen since its genesis, such as to the scope of its activities. Perhaps this extract from the January 1995 (Issue No. 1) of the *Bulletin* will provide a little more insight (**Figure 1**). The then editor, Rupert Purchase, only retired from the committee in recent years, and remains a contemporary contributor.

Further insight into changes in environmental chemistry over the years is provided by David Owen (**pp 16-17**), whose reflections throughout his career capture our rapidly-changing understanding of environmental chemistry across water, atmospheric, and industrial sectors.

Rowena Fletcher-Wood
ECG Chair and *Bulletin* Executive editor



Past

From its inception in the early 1970s until 1994, the Environment Group operated as part of the RSC's Industrial Division. During this period environmental chemistry has grown and matured into a scientific discipline in its own right, and many of our 2000+ members are active in developing the chemistry of environmentally-related subjects.

As a reflection of this change of emphasis, in 1993 the Environment Group Committee sought and received the members' approval to change the Group's name to the Environmental Chemistry Group and to switch our affiliation to the Society's Scientific Affairs Board.

Objectives of the Environmental Chemistry Group

- to organise technical symposia on environmental, health, and safety related topics;
- to maintain an awareness of current environmental issues and their underlying macro-chemistry;
- to publish developments in environmental chemistry using the resources of the RSC; and
- to provide technical support and advice to the Society's Professional Affairs Board and its Environment, Health and Safety Committee on environmental chemistry

Figure 1. Extract from Issue No. 1 Environmental Chemistry Group Newsletter (January 1995).

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The *ECG* Interview: Tomás Sherwen

Tomás Sherwen is a Research Scientist at the National Centre of Atmospheric Science at the University of York.

What inspired you to become a scientist?

I have always loved being outdoors since my childhood, growing up with my mum, who was a shepherd. The world around us captivates me. The further you dig into things, the more interesting – and complex – they become. This questioning and my drive to explore unknowns definitely moved me towards science.

How did you come to specialise in atmospheric chemistry?

I took a meandering route, gaining experience working in industry, non-profit, and research chemistry before choosing a PhD and then a job in atmospheric chemistry. My first proper taste of research was after winning a scholarship in green chemistry in my first undergraduate year. This, and internships in following summers, gave me an idea of what you could do with a degree in chemistry and an interest in environmental chemistry. Atmospheric chemistry gave me a way to pair up a fondness for working with computers and data analysis with the big challenges that humans face.

Could you describe your current job?

I use numerical models to explore questions about the chemical composition of the atmosphere now, in the past, and going into the future. Most of my day-to-day work is spent wrangling and plotting data, exploring differences between models and observations, and working on problems with people all around the world.

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

I'd focus on fundamentals first, then specify later. Experience of different sectors through internships/placements helps you find out what you like (and don't!).

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

We are working out how to embrace new computing resources and techniques, using science to mitigate the global burden of pollution, and making sure science is translated broadly into impact, whilst counteracting the widespread (and sometimes active) sources of disinformation. Addressing some of these challenges could have significant positive impacts.

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

It is definitely the people and the experiences. I've been lucky to work in the USA, growing my analytical data skills within a newly developing field of data science, and been a mission scientist guiding where a plane laden with scientific instruments flew off the west coast of Africa. I really enjoy how collaborative my area is, which has really emphasised that science takes many people and many steps to succeed in increasing our knowledge.

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

I would be working on projects linked to engineering; designing and building homes that allow people to live enjoyable, affordable, and sustainable lives. For years, I have been fascinated by how we can improve the way we live whilst reducing our impact on the environment. Through two personal renovation projects, I have learned that much of the technology and knowledge already exists and I'm keen to help others find this too.

And what do you do when you are not working?

I am generally not very good at staying still… and so I am likely to be found outside sailing, windsurfing, walking, or whatever new hobby I can find. The most recent new hobby I've found is ice-axe climbing, and I'm looking forward to my next trip!

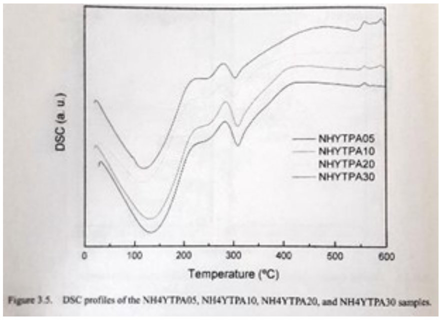
Book Review

Advanced oxidation technologies: Sustainable solutions for environmental treatments

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

This collaborative book provides an overview of Advanced Oxidation Technologies (AOTs) and a few Advanced Reduction Technologies (ARTs) "as sustainable, low cost and low energy treatments for water, air and soil".

Following editor profiles (Marta I. Litter, Roberto J. Candal, and J. Martín Meichtry), the book commences with the simplest technique reviewed – decontamination by solar irradiation. This comfortable, non-specialist introduction set the tone of the chapters to come. A uniform layout includes an introduction describing the principles, benefits, and drawbacks of the reviewed AOT, and environmental factors contributing to efficacy and efficiency of the technology. Where significant, target compounds were presented with their environmental relevance. Experimental sections discussed sample collection and preparation, AOT methods, and analysis techniques, and relevant photos were shown of apparatus and samples, condensing large volumes of useful experimental information. Results and Discussion (sometimes separate sections), follow and on occasion take into account the potential negative impacts of the AOT, including reaction intermediates, by-products, and potentially harmful effects of interactions, ensuring that readers looking to evaluate the suitability of an AOT for a desired application are able to consider these factors. Conclusions on the suitability of the AOT for the treatment applications investigated were presented last.



Reproduced with permission from Marchena, C. L. et al. Chapter 3 – Synthesis, characterisation and catalytic evaluation of tungstophosphoric acid immobilised on Y zeolite .

Efficiency, sustainability, and cost-effectiveness were evaluated, keeping in mind the real-world applications of these methods. All but two of the 19 treatments addressed water pollution, covering the general decontamination of water, water splitting for hydrogen gas and the removal of compounds including arsenic, azo dyes, phenol, herbicides (e.g. glyphosate), perchlorate, insecticides (chloropyrifos), nitrates (from fertilisers/industrial effluent), organophosphates (pesticides), bacteria (*E. coli*), and pharmaceuticals (β-blockers). The majority of test data come from water samples but some techniques are applicable to soil runoff. Air pollution treatments addressed the presence of bacterial endospores from indoor air pollution, and NO_x/volatile toluene gases from fossil fuels.

At relevant points throughout, the chemical reactions, interactions and degradation mechanisms are presented for each AOT, highlighting the effective pathways of the treatments. Some chapters address operational variables of the technique (light, temperature, etc.), whilst others assess different active components or methods for their synthesis. Where intermediates and by-products are identified as potentially hazardous or harmful to human health or the environment, this is assessed, including ecotoxicity assays. Data is supported by abundant charts and figures, but some information is lost in monochrome print (figures referred to "red lines"). The final chapter provides an excellent review of similar techniques and selection of the most applicable.

Some of the acronyms and abbreviations used present a possible source of confusion due to their similarities with chemical formulae (e.g. CoI is not an erroneous reference to CoI_2, but reference compound I). There are several proofing and translation errors.

Overall, this book is an excellent resource for anyone looking to gain insight into the applications and implementation of AOTs. However, it is not accessible to the layperson (non-chemist). I would recommend this book to any interested graduate chemist and certainly to chemists looking to identify different methods for cost-effective and energy efficient treatment of polluted waters.

Reference

Litter, M. I., Candal, R. J. and Meichtry, J. M., 2017. *Advanced Oxidation Technologies: Sustainable Solutions for Environmental Treatments.* CRC Press, Leiden, NL. ISBN: 9781138072886.

Review

Presentation training – Duncan Yellowlees

Rowena Fletcher-Wood (Freelance science communicator, rowena.fletcherwood@gmail.com)

Duncan Yellowlees is a presentation coach and "rockstar when it comes to helping out with presentations" (according to his reviewers). He specialises in academic storytelling and narrative training, working with universities and institutions to help speakers "not be rubbish". His informal, humorous, and highly energised presentation and delivery skills workshop is reviewed here.

Mr Yellowlees is a fan of Dr Gallagher's delivery style (reviewed in *January 2021 Environmental Chemistry Group Bulletin, pp5*), and I can see the influence: the workshop began with hold music and instructions establishing his preferred view format. Live captions, transcripts, and a private recording for those with an unstable connection were used to improve accessibility. Nevertheless, he might have improved it further by making the text on his slides larger and closing them when not in use.

Having heard Mr Yellowlees speak elsewhere, I expected the session to be highly engaging – it was. Using preconised voice modulation techniques, and interweaving narrative examples, he stood throughout the two-hour session, including the ten-minute tea break, which became an impromptu additional Q&A. Participants were invited to use two text media (Zoom chat and Slido). I was sceptical of Slido, since Mr Yellowlees implied that it was not straightforward by repeatedly mentioning possible connection challenges, but did not test it. Participants were not invited to unmute themselves to speak (although some did). The session would have benefitted from an introduction to tools and engagement expectations.

The **introduction** began with the story of an ice cream van distracting a player during a game of catch, an analogy for two-way engagement. It warned us of the challenge trying to play catch with a disinterested partner (the audience). I was unsure whether Mr Yellowlees' nervous delivery of the punchline was accidental, or a clever tactic to build relatability. He moved on to other connection-building steps, such as using the names of participants and admitting to one's own presentation faults. The first 25 minutes comprised of staple reflective presentation training questions, like what percentage of talks are inspiring? What makes a good (or bad) presenter?

The three main components of the training were presented in a novel "choose your own adventure" format. During voting, Mr Yellowlees maintained the energy in the room by commenting on the progression of dynamic results. We first voted for **emotions**, covering the flattening effect of being on stage or speaking on Zoom, the importance of voice variability ("the Goldilocks rule"), and contagiousness of speaker emotions. Mr Yellowless gave exercises for amplifying emotions (perhaps poorly suited to Zoom, but useful tools for later practice). The section could have benefitted from specific techniques, e.g. "faking" emotions.

We moved on to **voice**. In my favourite take away from the workshop, Mr Yellowlees invited us to "stretch, shrink and play" with words and have fun presenting. He described a PhD as "knowing more and more about less and less" and how this led to the evolution of a specialist language, rich with exclusive jargon. Discussion centred around the examples offered by participants (acronyms), but nevertheless I would have enjoyed mention of 'unexpected jargon', e.g. the word "species", not used colloquially as it is in chemistry.

In **body language**, Mr Yellowlees came into his own. A specialist in desktop delivery, his unique contribution to presentation training included online-specific guidance and technological suggestions, including how to align your eyes with the camera to appear warm, techniques for posture and moving the upper and lower body, camera types, volume, and use of presenter view.

To close the workshop, Mr Yellowlees provided another story: being chased by a tiger. He demonstrated why nervousness leads to irrational expectations of the audience as ravenous canines. But most are empathetic. He provided a few straightforward tips for managing nerves (such as visualisation and diverting focus), with reference to theories and other experts. Although this training could have benefitted from recent research, Mr Yellowlees was a highly personable trainer presenting a well-paced and robust workshop. Nevertheless, as a storytelling specialist, I would have liked to have seen the end catch us and throw us back to the start and complete the journey.

Resources

https://www.duncanyellowlees.com

Article

Accessing powerful nanostructures of exfoliated biochar using green solvents

2021 #RSCPoster Twitter Conference
2 March 2021 12:00 - 3 March 2021 12:00

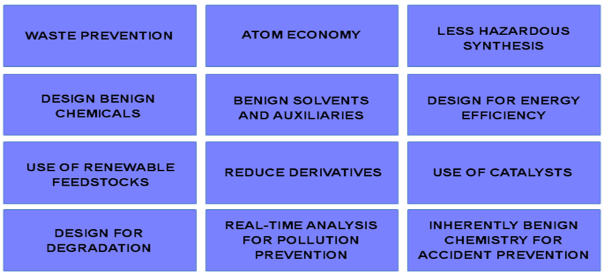
Juliana Vidal (Memorial University of Newfoundland, jlvidal@mun.ca)

By the 90s, environmental concerns led to the formulation of the principles of Green Chemistry, which involve the design and/or modification of chemical processes and products to minimise (or ideally eliminate) the use and generation of hazardous substances (*1*,*2*). Green Chemistry can help in the achievement of the UN's 2015 Sustainable Development Goals (SDGs) and has become a profitable strategy for preserving the future of our planet (*3*). Yet how can we develop green products that are also successful in the marketplace?

To solve this challenge, John Warner and Paul Anastas created, in 1998, the 12 Principles of Green Chemistry (**Figure 1**), a holistic guiding framework for chemistry to provide benefits to our society without harming human health and the environment (*2*).

Biochar and sustainable development

Large amounts of wood waste are generated by paper mill industries and sawmills. The majority of the sludge, bark, and sawdust produced are transported to landfills or abandoned on the harvested sites, liberating greenhouse gases to our atmosphere during decomposition. If we use pyrolysis to transform the biomass waste into biochar instead of leaving it aside to decompose, the environmental problems of their decay can be mitigated while producing useful materials and energy (*4*).



WASTE PREVENTION	ATOM ECONOMY	LESS HAZARDOUS SYNTHESIS
DESIGN BENIGN CHEMICALS	BENIGN SOLVENTS AND AUXILIARIES	DESIGN FOR ENERGY EFFICIENCY
USE OF RENEWABLE FEEDSTOCKS	REDUCE DERIVATIVES	USE OF CATALYSTS
DESIGN FOR DEGRADATION	REAL-TIME ANALYSIS FOR POLLUTION PREVENTION	INHERENTLY BENIGN CHEMISTRY FOR ACCIDENT PREVENTION

Figure 1. The 12 Principles of Green Chemistry.

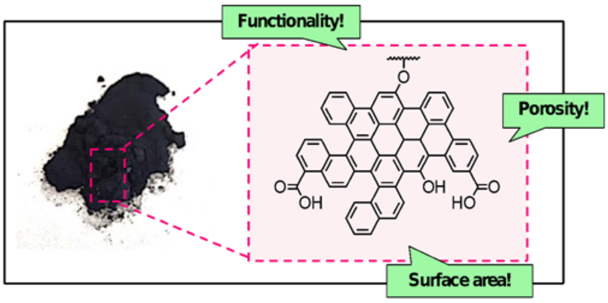


Figure 2. Representative fragment of the biochar structure.

Pyrolysis is the thermochemical decomposition of organic matter in an inert environment (i.e. in the absence of oxygen) in the temperature range typically 400–800° C. Through this treatment, waste biomass is transformed into biochar, a material that decomposes more slowly than wood or other forms of biomass (*5*). This process has the potential to mitigate carbon dioxide (CO_2) emissions and climate change by rerouting carbon from a rapid biological cycle to a much slower cycle (*6*).

The role of biochar as a carbon sink has been recognised by the Intergovernmental Panel on Climate Change (IPCC) in their 2014 report (*7*). Bio-oil and syngas are also produced during pyrolysis, and can be used as sources of renewable energy.

Biochar is a carbon material of high porosity, surface area, and surface functionality **(Figure 2)** (*8*)**.** It is mainly used to remove pollutants from aqueous solutions and improve soil fertility. An increase in the utilisation of biochar in higher value-added fields not only represents an important approach in terms of climate change mitigation, but can also help to promote economic growth whilst reducing impacts of consumption.

Making exfoliated biochar greener

Layered materials are solids with strong in-plane bonds and weak interactions between layers. Through a process known as exfoliation, those weak interlayer attractions may be broken using external force, thus producing a single or a small number (< 10) of stacked nanosheets (*9*). When the material is immersed in a

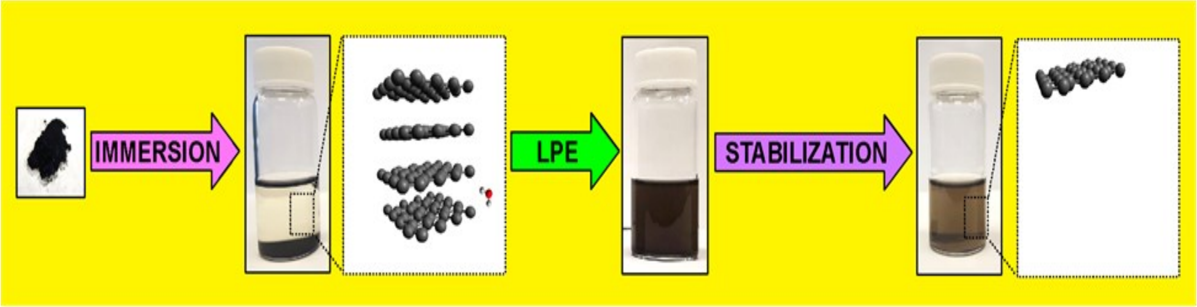


Figure 3. The mechanism of the Liquid Phase Exfoliation (LPE) of biochar.

solvent and ultrasound applied as an external force, the process is then called Liquid-Phase Exfoliation (LPE) (**Figure 3**) (*10*). Biochar nanostructures (nanobiochar) obtained by LPE of biochar possess enhanced physicochemical characteristics when compared to layered counterparts. Nanobiochar incorporated into other materials increases the commercial value of these products (*11*). The LPE of biochar and other carbon materials has been described in the literature (12-15). Solvent parameters such as surface tension and density play an essential role in the process (*16*). For example, if solvents with the appropriate properties are used, LPE is more efficient and requires less energy. The most commonly used solvent for LPE is *N*-methylpyrrolidone (NMP); an expensive, high-boiling point (202 °C), and toxic solvent. The mechanisms underpinning solvent selection for the LPE of biochar remains unclear. Our objective was to understand better these mechanisms and to identify benign alternative (green) solvents for the production of exfoliated biochar (*17*). Besides surface tension and density, we discovered that another set of solvent properties, known as Kamlet-Taft solvatochromic parameters, were responsible for facilitating the process. Depending on the hydrogen-bonding ability and polarisability of the solvent, samples could efficiently exfoliate biochar and its oxidised analogue from different biomass feedstocks (*i.e.* from hardwood and softwood trees). Moreover, biochar nanostructure samples containing between 2-8 layers (~ 15 nm thickness) could be produced in greener alternative solvents than NMP with similar yields. These alternative solvents include dimethyl carbonate, ethyl acetate, polyethylene glycols, and ε-caprolactone.

Conclusions

Nanobiochar can be used to improve the physical and mechanical properties of composite materials. The biochar nanostructures described in this study have potential use as fillers in the manufacture of cheaper biodegradable, non-fossil fuel derived, biocomposites.

We hope the work described here will encourage others to evaluate different solvents and mechanisms for the LPE of layered materials – thus developing the application of biochar and helping to implement the Twelve Principles of Green Chemistry.

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The #RSCPoster Twitter Conference is an annual online event to bring the research community together over just 24 hours. In 2021, c 900 submissions were received from 62 countries, with 5,500 people discussing them on Twitter. Juliana Vidal was the RSC poster winner.

Article

Synthesis of spherical TiO_2 microspheres to degrade rifampicin

2021 #RSCPoster Twitter Conference

2 March 2021 12:00 - 3 March 2021 12:00

Paul. K. Kimani (Gifu University, Japan, paulkimani90.pk@gmail.com)

Pharmaceutical and personal care products (PPCPs) are an emerging group of contaminants of increasing environmental concern. They are mostly synthetic organic chemicals used to treat various animal and human diseases. Extensively and widely used, they are vital to economies, but end up accumulating in ecosystems via food webs where they pose health-related threats as they are naturally bioactive and are linked to increased cases of ecotoxicity and antimicrobial resistance.

PPCPs find their way into the environment through direct or indirect human excretion such as sweat, urine and faeces that end up in wastewater due to incomplete removal. Recent studies have shown an increased occurrence of antibiotics in water systems, and thus rising demand for mitigation. Various methods have been utilised to remove these pollutants such as coagulation, flocculation and ion exchange, which are, at times, costly. While processes such as membrane bioreactors (MBR) and enzyme-based biocatalysts are still under development, degradation via metal oxides remains cost-effective, efficient and more environmentally friendly.

Rifampicin is one PPCP that has been widely detected in the environment. A semisynthetic broad-spectrum antibiotic produced from *Streptomyces mediterranei*, it produces activity against forms of mycobacteria. It inhibits DNA-dependent RNA polymerase activity by forming a stable complex with the enzyme. 30% is usually excreted in its active form.

Titanium dioxide, TiO_2, microspheres were selected and synthesised via a sol-gel process. An aqueous solution of titanium tetrachloride, $TiCl_4$, was reacted with a 1.5 M solution of urea, forming titanium dioxide microspheres. These were characterised via Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) fitted with an Energy Dispersive X-ray spectrometer (EDS), and X-ray diffraction (XRD). Characterisation showed spherical anatase TiO_2 microspheres with sizes ranging from 200–2000 nm.

Comparative degradation studies were performed using the microspheres in the absence or presence of hydrogen peroxide (H_2O_2) and at different pHs to determine optimum degradation conditions. An aqueous solution of 50 µM rifampicin was prepared from which 3 mL were mixed with 10 mg of microspheres and 1 mL of hydrogen peroxide for the degradation, which was studied at 2 min intervals using a Shimadzu 1800 Ultraviolet-visual (UV-vis) spectrophotometer in the

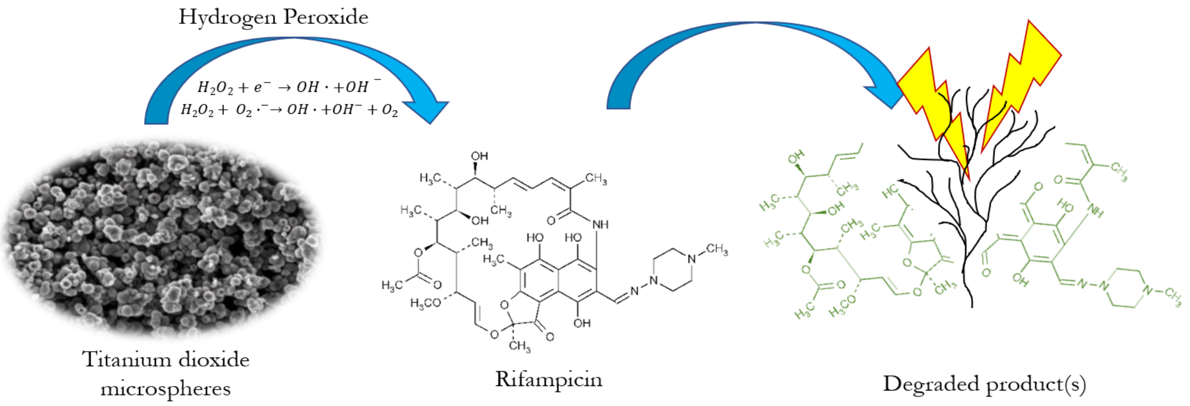

Figure 1. Degradation of rifampicin using TiO_2 microspheres.

range 300–800 nm. Longer extraction times were required to degrade rifampicin when either H_2O_2 or TiO_2 were used independently, compared to 120 minutes required when used together.

This shows the importance of TiO_2 in the generation of radicals that assist in the degradation process. This rate of oxidation was further improved by adjusting the pH to 3 or pH 12 with the highest percentage removal (63.8%) at pH 12. The degradation follows a first-order mechanism with the rate higher in acidic media as compared to neutral or basic media.

Further research will study the products of degradation to verify non-toxicity.

Reference

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The #RSCPoster Twitter Conference is an annual online event to bring the research community together over just 24 hours. In 2021, almost 900 submissions were received from 62 countries, with 5,500 people discussing them on Twitter.

For more information and to find out more about sponsors and poster winners, visit https://www.rsc.org/our-events/rsc-poster/

OXFORD SCIENCE
+IDEAS FESTIVAL

Call for outreach volunteers!

IF Oxford is running a potentially in-person science event on 9-10 October 2021, and the ECG are recruiting volunteers to support their table-top stall themed on ocean acidification and air quality monitoring. To participate in the Oxford event, or find out more, email rowena.fletcherwood@gmail.com.

Volunteers will be trained, and lunch and travel expenses will be provided.

Do you have an idea for a demonstration?

If you'd like to support our outreach with ideas for a family-friendly table-top demonstration on ocean acidification or air quality.

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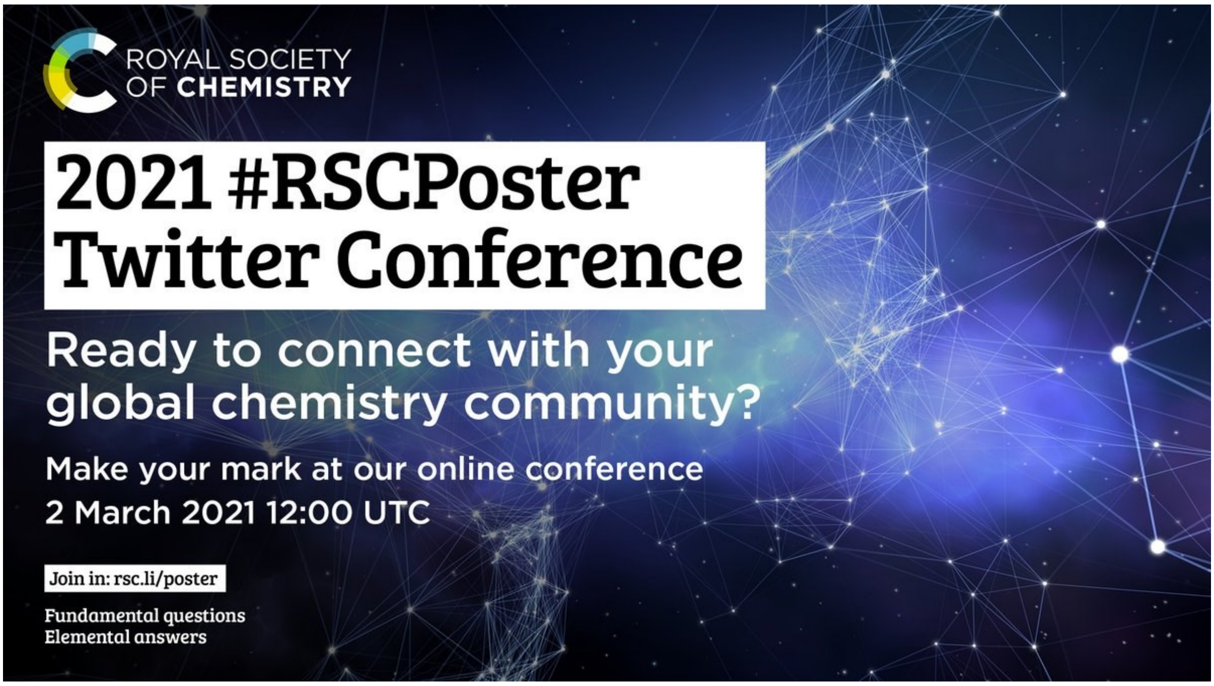

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Fundamental questions
Elemental answers

Article

Natural analogues for nuclear waste: a window into the future?

Clare L. Thorpe, Claire L. Corkhill, Russell J. Hand (University of Sheffield)

Glassy materials – those with no long-range atomic structure – are ubiquitous in our modern lives. Glass is formed when a molten liquid cools rapidly. Although many substances can be induced to form a glass, few do so as readily as silica (SiO_2), making silicate glasses the most common. Other elements may substitute into the glass structure, either as covalent network formers (e.g. B and Al) in place of Si, or as network modifiers (e.g. Na^+, K^+, Ca^{2+}, or Fe^{2+}) that form ionic bonds with oxygen from the silicate network.

The addition of other elements to silicate glass has a variety of effects, such as lowering melting temperatures, improving physical or chemical durability, and changing the colour of the glass. The longevity of glass across a range of natural environments is of interest from the point of view of building construction, the manufacture of components such as semiconductors and fibre optics, the preservation of art and archaeological artefacts, and the safe disposal of vitrified waste. The impetus to understand glass degradation over very long time periods (> 10,000 years) primarily arises from the need to ensure that vitrified radioactive waste emplaced in subsurface disposal facilities will not pose a hazard to future generations.

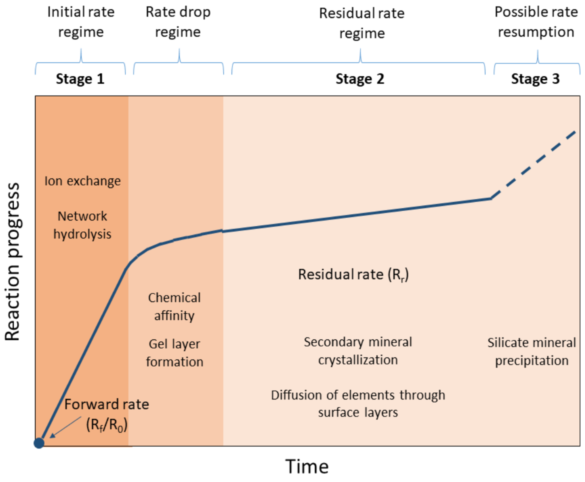

Figure 1. Accepted mechanism for glass corrosion.

In the UK, and in many countries including the USA, France, Russia, Germany and Japan, high level radioactive waste is formed from reprocessing spent nuclear fuel. This waste is immobilised by vitrification in a borosilicate glass matrix and destined for eventual disposal in an engineered geological facility. Vitrification is also being considered for lower radioactivity waste streams due to the wide range of elements that glass can incorporate, its chemical durability and resistance to radiation damage. Prior to geological disposal, the glass waste form is usually contained in a steel canister designed to keep the waste isolated from groundwater ingress for tens to hundreds of years, even after the surrounding backfill materials and geological units become saturated. However, radioactive waste needs to be isolated from the biosphere for thousands to tens of thousands of years (depending on the radioisotope in question) to allow the radioactivity to decay to safe levels. The rate of corrosion of the glass matrix is therefore an important factor in the safety case for disposal of vitrified radioactive wastes.

There is scientific consensus that glasses start to corrode when in contact with water or water vapour, and that the general mechanism begins with ion exchange between H^+/H_3O^+ from the water and alkali metals (e.g. Li^+, Na^+, K^+) from the glass. Concurrently, hydrolysis of the glass network leads to the breakdown of Si-O and B-O bonds (*1*). Elements released from the glass accumulate in solution until sufficient silica is freed to allow the formation of an amorphous gel layer on the glass surface. This layer densifies over time and can crystallise into secondary mineral phases (*2*), meaning that further corrosion of the bulk glass is limited by the diffusion through this surface alteration layer and the rate of release of elements from the glass decreases (**Figure 1**). The rate of glass dissolution can continue at this reduced rate indefinitely, or, under some conditions, the precipitation of certain minerals, for example zeolites, can drive an increase in the glass dissolution rate (*3, 4*).

Although the glass corrosion mechanism is well established, rates and timescales remain unpredictable, as the progress of glass degradation is dependent on a number of factors including pH, temperature, glass composition and solution chemistry. The rates of glass corrosion increase with increasing temperature and extreme pH conditions (either acidic or alkaline) can promote hydrolysis of the silicate network. The initial durability of the glass is highly dependent on its chemistry, with more polymerised networks – those with more 'bridging' oxygens – showing the greatest durability. Additionally, both the solution chemistry and glass chemistry can greatly influence the composition of the gel layer formation and secondary mineral precipitates.

Figure 3. Example of manmade glasses that have been exposed to aqueous environments.

To date, most estimates of glass corrosion rates have been derived from accelerated laboratory tests. In order to achieve measurable results over a short time period, laboratory tests are accelerated by increasing the glass surface area and raising the temperature, often to $\geq 90\ ^{0}$C. In addition, processes that occur only in complex natural environments and are not observable in simplified, sterile laboratory tests may influence corrosion. These include the direct and indirect effect of microbial metabolism, the effect of changing or fluctuating geochemistry, and variable saturation which are, as yet, poorly understood.

Natural and archaeological analogues

One way to validate the results obtained from static laboratory testing is by comparison with natural and ancient glasses that have been exposed to a known environment for a known period. These samples have come to be termed 'natural analogues'; their behaviour provides an analogue for that of modern nuclear waste glasses that have only been manufactured in the last 50 years.

Natural glasses include igneous glasses of basaltic (rich in Fe and Mg) and rhyolitic (rich in Si) compositions, fulgurites (petrified lightning strikes), glass observed in meteorites and impact glasses (**Figure 2**).

Ancient glass samples include those found at Roman and Medieval burial sites, the walls of vitrified Hill Forts, and those retrieved from shipwrecks where the start date of their contact with water or soil can be well constrained (**Figure 3**). These sources provide a surprising range of glass compositions from soda-lime and lead silicates used to make bottles and decorative artefacts to metal-rich vitreous slags formed as by-products from copper smelting.

The major limitation when comparing the dissolution of natural or ancient glasses with that of nuclear waste glasses lies in compositional differences and, notably, the absence of boron. Boron oxide (B_2O_3) is included in most nuclear waste glass composition at 5-25 weight %, where it substitutes into the silicate network and improves chemical durability. As borosilicate glass was only commercially manufactured from the early 1900s and nuclear waste compositions only from the 1970s, there are no older samples available to study. Therefore, purposeful long term burial experiments have been established under a variety of conditions relevant to geological waste disposal, including in different geological lithologies (granite, salt, limestone and clay) (*5-8*). Sometimes referred to as 'field tests', these studies aim to bridge the gap between precise, short term, laboratory studies and observations from natural analogue studies where differences in glass composition and exact environmental conditions may lead to uncertainty.

Figure 2. Examples of naturally formed silicate glasses. Samples were photographed from the Manchester Museum Collection.

Figure 4. Left, location of the Ballidon Long Burial Experiment; middle, weather monitoring equipment on top of the burial site; right, summary of glass to be unearthed in 2022.

Figure 5. Left, location of Peak Dale; middle. Images of the cave ad calcium rich precipitates;

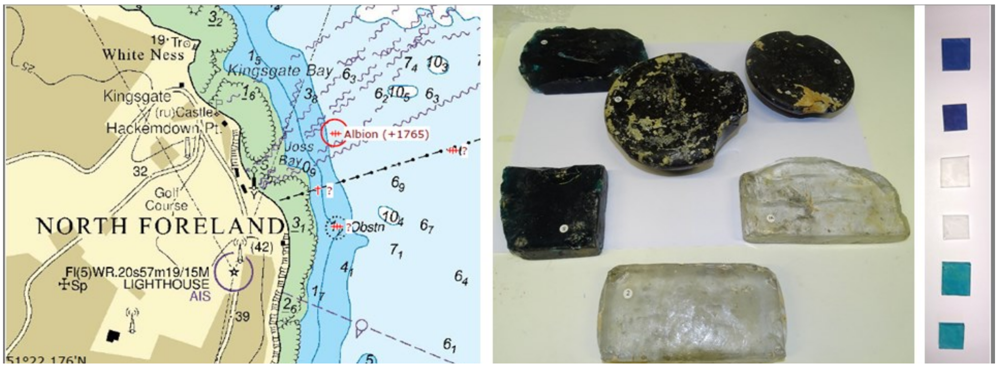

Figure 6, Left, location of the shipwreck of the Albion where the cglass ingots were found; middle and right, images of the ingots colored ble (Co), clear (Mn) and green (Cu).

Figure 7 Left, location of Haye, Cornwall, UK; middle, a vitreous slag sample; right, slag sample held in position for 250 years by inclusion in a bridge across Hayle estuary.

UK example studies

The University of Sheffield Immobilisation Science Laboratory specialises in developing new thermal treatment solutions for radioactive wastes and in assessing the long term durability of both new and existing vitreous waste forms. A number of natural analogue studies are underway to complement laboratory-based dissolution testing and investigate glass corrosion in complex natural environments.

Ballidon long-duration experiment

The Ballidon Quarry, Derbyshire, UK, hosts one of the longest running glass burial experiments in the world (**Figure 4**). Now in its 50th year, this site was originally established to test the degradation of archaeological glasses under alkaline conditions compared to a sister experiment in acidic soil (*9*). Later, simulant (non-radioactive) nuclear waste glasses were added to the experiment, along with climate monitoring equipment to ensure conditions at Ballidon are well constrained before the next set of samples are removed in 2022.

Peak Dale Cave

In Peak Dale, Derbyshire, UK, a man-made tunnel beneath a lime workings provides a stable environment with hyperalkaline, Ca-rich water chemistry analogous to the cement leachates expected to evolve over time within a geological disposal facility where a cementitious engineered barrier is used. In addition to analysing glass samples found in the cave estimated at > 70 years old (the date the tunnel was closed) (*10, 11*), researchers at the University of Sheffield have established a new field test including nuclear waste glass compositions from the UK and USA set to run for 30 years (**Figure 5**).

Albion shipwreck glasses

Analysis of 265 year old unique glass ingots (**Figure 6**), from a marine environment allows a low temperature corrosion comparison. Samples show evidence of biological colonisation and provide an opportunity to assess the effect of minor metal constituents of the glass (e.g. Cu, Co, and Mn), which were added as colourants but may also have biocidal effects. This work is funded by the Royal Society of Chemistry Research Fund.

Black Bridge slag samples

Archaeological vitreous slag samples found within the town of Hayle, West Cornwall, may provide a close natural analogue to some heterogeneous glasses produced from mixed wastes such as plutonium contaminated materials (**Figure 7**) (*12, 13*). The Copperhouse foundry, first founded in 1758, and the Black Bridge, constructed circa 1811, can be used to date Hayle slag samples as ~ 250 years old. As the slag blocks were fixed in position, their exposure environment is known: depending on location, they were exposed to saline water, brackish water, or rainwater. A new study plans to investigate the corrosion of these materials and slags from other locations as an analogue for iron rich nuclear waste glasses.

Conclusions

No single natural analogue or field test site can tell us everything we need to know about the long term behaviour of glass. However, using a combination of many can increase our understanding of corrosion mechanisms under a wide variety of environments and decrease the margin of uncertainty around elemental release from vitrified radioactive wastes.

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Article

Paper-origami devices for COVID-19

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Pathogen detection is significantly important for both infectious disease diagnostics and wastewater surveillance. The current gold standard method for pathogen detection is the polymerase chain reaction (PCR), but it requires centralised facilities and skilled personnel. There is thus an urgent need to develop rapid and sensitive platforms for the identification and quantification of pathogens. Here, we present a low cost and deployable paper-based device for detection of pathogens in both clinical and environmental samples including field testing of infectious diseases (e.g. malaria), and testing wastewater for early warning of the pandemic (*1*).

Paper for rapid diagnostics

The paper-origami device was initially developed for testing of bovine infectious reproductive diseases, which enabled a multiplexed, and sample-to-answer paper-origami test to identify bovine herpes virus-1 and two bacteria from semen samples in rural India and was able to measure < 1 pg of target genomic DNA (**Figure 1A**) (*2*). The device also allows for genetic material extraction and purification, which in combination with isothermal amplification and lateral flow detection enabled rapid diagnosis of malaria DNA in less than 50 minutes (**Figure 1B**) (*3*). It has been field-tested in Uganda to show a promising sensitivity and specificity.

Wastewater-based epidemiology

Wastewater-based epidemiology (WBE) has shown to be a powerful tool for early warning of infectious disease including SARS-CoV-2, which enables the analysis of biomarkers from wastewater to understand health information at the community level. We developed a paper-based lateral flow device to quantify human-specific mitochondrial DNA (mtDNA) in wastewater, providing a rapid method for monitoring genetic biomarkers (**Figure 1C**) (*4*). For example, the infectious respiratory disease caused by SARS-CoV-2 has evolved into a global pandemic and the paper-based device is becoming a rapid tool to test wastewater for early warning of the outbreak within the support of a UK national COVID-19 wastewater epidemiology surveillance programme (N-WESP).

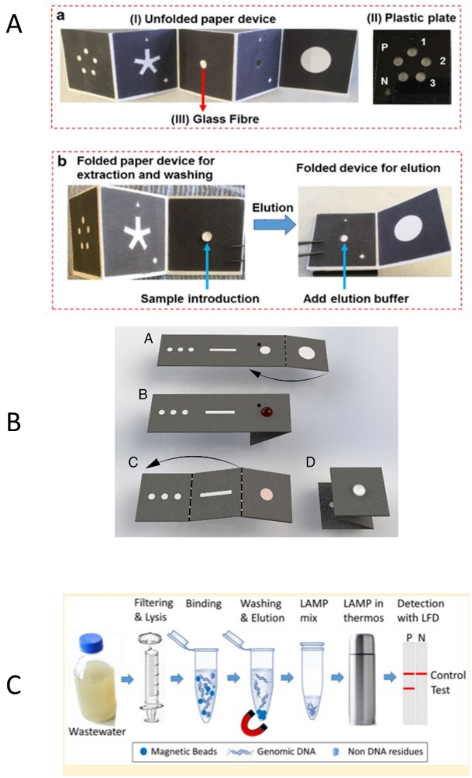

Figure 1. Origami paper-based device.

To sum up, paper-based devices are cost-effective, highly selective, sensitive, portable, and easy to use. They provide a rapid platform for both individual diagnosis and sewage testing for public health assessment (*5*). The device also has the potential to be integrated as a point-of-care biosensor system with mobile health for wastewater-based epidemiology (iBMW) for early warning of COVID-19 and other infectious diseases, screening and diagnosis of potential infectors, and improving health care and public health (*6*).

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Article

From the 1970s to today: A view on environmental progress

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David Owen reflects on his career in chemistry, exploring how initially environmental chemistry was primarily concerned with the development of control techniques to comply with emerging environmental legislation.

About the author

David Owen has an organic chemistry background; his first degree was from Liverpool University. He worked with Lucas in Birmingham as a development chemist in the motor vehicle battery industry and subsequently received a PhD in organo-fluorine chemistry from Birmingham University. After working for British Steel for three years, he joined Betz Laboratories, an American water treatment company with a spread of interests, set up the Irish operation and resided in Ireland for four years before setting up his own business specialising in wastewater management and its chemistries. Specialist areas included paper chemistry and refinery equipment decontamination during turnaround maintenance. He later established a new chemical company, marketed towards waste management in the oil industry (drilling fluid management) and in refinery process waste streams. He continues to consult on specific industrial problems and serves on the RSC ECG committee.

I spent my early working years in industry working at an American company specialising in water and process chemistry. Their target market was large process industries in continuous operation: hydrocarbon processing (refining); exploration (downhole); chemical plants (*e.g.* ammonia or urea, monomers for plastics such as ethylene and styrene); steel; mining (especially coal); metal industry (*e.g.* bauxite purification and aluminium production); and paper. Other miscellaneous industries included fibre production from cellulose or man-made raw materials. This work gave me precious expertise in a variety of industry practices and processes; I will discuss some of them here. After understanding utilities and processes, which were the beating heart of their operations, more detailed analyses turned to corrosion control in cooling water, boiler-water treatments to ensure optimum heat transfer and cleanliness of the water and equipment furnaces."

Water industry

In the late 70s, the major concern was environmental compliance, especially effluent waters. Suspended solids, oil in water, COD (chemical oxygen demand) and chemicals became the main source of anxiety. At the time, it was common to use chromate-based corrosion inhibitors in large cooling water systems. The reason? Because they worked well. The wastewater then went down the drain untreated. Some plants were using several tonnes of chromate per year. This was the substance that caused cancers in California, as depicted in the film *Erin Brockovich*, a landmark case in environmental law. Aided by technology advances, chromate was phased out in the mid-80s. Indeed, many substances used for various industrial applications were either banned outright or substituted in the 80s. For example, hydrazine was used as an oxygen scavenger in high pressure boilers. The material was shown to be mutagenic and new technology was introduced to prevent exposure."

Atmospheric chemistry

During my PhD, studies into organo-fluorine chemistry, the hole in the ozone layer finding was discovered. Chlorofluorocarbons (CFCs) were blamed, and the Montreal Protocol ended their manufacture in the West. China continued to manufacture CFCs long after replacements were found. Fluorine chemistry was seen as the sole bad actor, although its products had been in existence for some time as aerosol propellants and as refrigerant gases.

Oil industry

At Birmingham University, one of my lecturers was seriously concerned about lead in petrol as an octane improver. He would tell anyone who would listen about the evils of the substance. He was a respected academic, but most people simply listened politely and shrugged.

In the UK, there was a pecking order between industries. Usually, the oil and petrochemical industries would clean up their act first with the installation of new effluent plants to deal with free oil in water, suspended solids and sometimes biological oxidation of pollutants in an oxidation ditch. Clean-up in other industries would follow. There was an industry based in Ellesmere Port next to the Shell petrochemical plant, that manufactured tetraethyl lead (TEL). Prior to being was phased out in 1999, it had been responsible for 74% of UK lead emissions from petrol. After phase-out, the contribution was just 1%. The manufacturer moved into new products, and seeing the redundant equipment from the manufacturing of TEL, the sense of 'why did it take so long' was overwhelming.

Steel industry

The steel industry was large, with five major sites operating blast furnaces and steel converter plants called BOS (basic oxygen steelmaking). This was known as the "heavy end". The making of steel required a large amount of metallurgical grade carbon in the form of coke.

A coke oven was an ecological nightmare, the coal was converted to coke by dry distillation of crushed coal at >1100°C. The gas produced was extremely crude and consisted of hydrogen, carbon monoxide, aromatics such as benzene, toluene and xylene (BTX), and it was rich in ammonia and tar. Other contaminants were cyanide and sulphide. The odour was unique and enveloped the local area. A by-product plant attached to each coke oven cooled and cleaned the gas to remove some of the contaminants. Huge steam plumes developed when these plants quenched the red-hot coke underwater. The clean gas was used to fire the ovens , with the remaining used to heat processes in the steel mill. Each of the operations were large units on vast sites. The main issues were fouling in off gas mains and equipment along with wastewater quality. Typical plants could produce about 40,000 tonnes of coke per week.

Most of this activity came to an end with the sale of the British Steel Corporation (BSC). Once in private hands, the corporation was downsized, and major steel works closed their "heavy end" forever. At one stage, BSC was making about 15 million tonnes of steel per year. The tonnage has been reduced with the closure of the heavy ends .

Coal industry

The coal industry existed in most parts of Britain; however, the problems of pollution were particularly severe in South Wales due to the narrow seams and the presence of fine clays near the seams. The excavated coal had to be crushed and washed to provide a clean product. The washeries designed to settle out the polluting clays failed badly and there was a high load of clay discharged to the local rivers. In the late 70s, products became available which caused the clays to floc into larger, settle-able particles. The lagoon systems began to work well, and this type of pollution effectively ceased. Now the problem has disappeared due to closure of all the pits.

Paper industry

The paper industry in Britain has had a chequered past. Local production was in three main centres: Kent, Northwest England and Scotland. There were some pulp mills working in the 70s and into the 80s, but the polluting nature of the chemical pulping of raw feedstock (trees) made the environmental compliance impossible. The other main factor was the price of energy; ~ 1 tonne of water is evaporated per tonne of wet laid pulp in the formation of a sheet of paper. The solution was a change in scale of operations and product type.

Recycling plants were devised and commissioned to recover good pulp to make recycled white paper. The removal of ink from used paper became an art form using washing and floatation technologies with special chemical additives to make the plants technologies work. One of the unmentioned wastes from the recycling from pulp to paper is the waste fillers, usually chalk or clay, along with the rejected short fibres and inks. This material represents a large waste stream, typically of the order of several hundred tonnes per day for a typical 300 tonne per day pulp plant on a dry weight basis. It is spread on land as a form of 'fertiliser' on farmland local to the mills. There has been no viable alternative route to a product to date although some significant trials at making construction board were carried out."

Agricultural industry

Another major pollutant is ammonia. It is estimated that about 75% of all chemical ammonia sources spread on agricultural land (as fertiliser) ends up in rivers and ultimately in the air, where it acts as an air pollutant. The chemical industry has optimised the manufacture of ammonia from atmospheric nitrogen via the Haber process. A typical modern plant can produce 1000 tonnes per day of ammonia and 1200 tonnes per day of urea from a purified natural gas source. The carbon footprint has been reduced but remains large. New technology is emerging to optimise nitrogen in fertiliser, designing them to provide exactly the amount of nitrogen the plant needs.

Conclusions

The most polluting industries have closed down in the UK over the last fifty years and been exported to less regulated areas of the planet, driven by politics, legislation, economic factors and consumer action. In the next industrial age, critical raw materials and utility products promise to be the focus.

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Activity sheet

Colour Changing Chemistry

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Make your own universal indicator in this classic kitchen experiment to test for acids and alkalis.

Acids and alkalis in the environment make a big difference. Acid rain dissolves rocks and harms plants. Excessive acidity in the oceans is eating away at our coral reefs and causing sea creatures to migrate. It's the job of environmental chemists to test the pH of samples and to investigate the effect on people and living organisms.

You'll need

Red cabbage

Cooking pot of water

Glasses

Instructions

1. Under supervision, boil the cabbage and keep the water (you can eat the cabbage).
2. Once cool, pour a little into glasses.
3. Add things from your kitchen to make different colours.

Try

Lemon juice
Vinegar
Bicarbonate of soda
Fizzy drinks
Sugar
...and anything else you can think of!

Challenge

Make a rainbow! Can you work out from the colours what is acidic and what is alkaline?

Reference

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Sulfur dioxide and nitrogen oxides during the COVID-19 pandemic

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While the effects of sulfur dioxide and nitrogen oxides are widely recognised and have been for many decades, their subsequent effects since the beginning of the COVID-19 pandemic follow unique trends. This Environmental Brief focuses on the difference in effects shown before and during the pandemic.

Sources

Sulfur dioxide (SO_2) is naturally released into the atmosphere in large quantities through erupting volcanoes, and by human activities such as combustion of fossil fuels and smelting of sulfur-containing mineral ores. In the UK, 236,900 metric tons of sulfur dioxide were released in 2018 alone, despite the general trend of yearly reductions in compliance with international agreements within the UNECE Convention on Long Range Transboundary Air Pollution (CLRTAP) and some Sulfur Protocols within the European Union (Queensland Government, 2020).

In the UK alone, around 2.2 million tons of nitrogen oxides are released each year, with 50% of these from motor vehicles and 25% from power stations.

Nitrogen oxides (NO_x) comprise both nitric oxide (NO) and nitrogen dioxide (NO_2) and, like sulfur dioxide, are produced both naturally and due to human activities. NO_x are produced naturally through lightning strikes and microbial processes in soils. However, they are largely produced by combustion processes involving nitrogen compounds and the combination of oxygen and nitrogen. In the UK alone, around 2.2 million tons of nitrogen oxides are released each year, with 50% of these from motor vehicles and 25% from power stations. Like sulfur dioxide, the trend for NO_X emissions in the UK sees yearly reductions; largely due to compliance with protocols such as the 1988 Sofia Protocol concerning the volume of nitrogen oxides emissions.

Impacts

It is well known that the major environmental role of atmospheric SO_2 and NO_x is in the production of acid rain and its subsequent harmful effects on the environment. This is an umbrella term indicating acidic precipitation, usually with a pH of between 4.2 and 4.4, containing sulfuric or nitric acid, falling from the atmosphere as either wet or dry deposition (*1*). When SO_2 and NO_x are released, they may react with water and oxygen in the atmosphere. Newly formed acidic precipitation may be transported long distances by prevailing air currents, creating problems not only for those close to emission sources, but possibly stretching over hundreds of miles (*2*). Wet deposition will fall from the atmosphere as rain, snow, or hail, while dry deposition will form in the absence of moisture in the form of particles and gases, later mixing with water during proceeding rainfall events. Acid rain can enter water systems, penetrate soils, and run across the surface via runoff water. This acidity can cause major ecological effects on bodies of water such as lakes and streams because acid rain slowly makes waters more acidic. Acid rain also causes harm to vegetated environments and impacts human health. Acid rain also causes harm to vegetated environments and impacts human health.

Aquatic environments Acidification of waters leads to a higher dissolution rate of aluminium from soils to waters, creating a toxic environment for aquatic animals. This is particularly apparent in aquatic organisms such as clams, which require a pH of 6 or above to survive, leading to their death in waters toxified by acid rain (*1*). Interconnected ecosystems suffer secondary impacts from this acid rain because species at the base of aquatic food chains decline in number; eventually being unable to support non-aquatic species.

Vegetated environments An abundance of aluminium released from the soils, along with essential nutrients such as calcium disappearing from soils impacted by acid rain, can cause vegetated areas to suffer immensely. These factors inhibit the ability of water being absorbed and taken up by trees and plants, and acidic rainfall can directly harm leaves, flowers, and needles. Acidification can leave vegetation in an unhealthy state due to an inability to absorb critical levels of essential nutrients, leading to a higher chance of disease and lower reproduction rates (*2*).

Human impacts Physical structures such as limestone buildings can be damaged by acid deposits, as may other structures such as cars. Health problems such as asthma and eye irritation may arise when acid precipitation takes the form of inhalable fog (*2*).

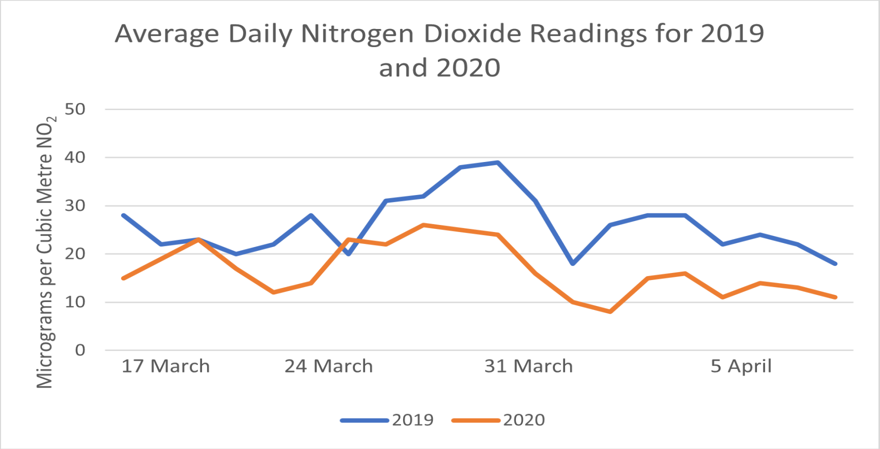

Figure 1. Graph comparing nitrogen dioxide levels between 2019 and 2020 showing over 50% reduction during lockdown, data from Khoo et al (3) .

Since the pandemic

During the countrywide lockdown in the United Kingdom imposed on March 23rd, 2020, anthropogenic movements were rapidly supressed. During the first 100 days of the lockdown, a significant reduction in air pollution levels were noted, compared to the same time period over the previous seven years. On average across the United Kingdom, NO_x levels were much lower for this period – approximately 50% lower – whilst SO_2 levels rose by over 50%. **Figure 1** illustrates the vast reduction of nitrogen dioxide levels recorded since the first day of the March 2020 UK lockdown, compared with data from the year before.

Data from the UK Department for Transport suggest that vehicle transport on the first day of lockdown was at 69% of its usual volume and, by April 13th, this had reduced to 23%. Since motor vehicle traffic accounts for the majority of the NO_x emissions in the United Kingdom, the 77% decrease in motor transport by April 13th led to a huge decrease in NO_x emissions. The decrease in NO_x and particulate matter during this time resulted in a positive effect on air quality, temporarily reducing the volume of NO_x available in the atmosphere to react with water and oxygen. This improvement in air quality reduced the volume of acidic precipitation in the UK, and nearby countries, improving the quality of aquatic and vegetated areas and temporarily benefiting human health by alleviating conditions such as asthma or eye irritations due to the reduction in acidic inhalable fog (*3, 4*). However, an increase of SO_2 emissions of over 100% has been observed during the March 2020 lockdown. Despite a reduction in motor vehicle traffic, SO_2 levels more than doubled across the United Kingdom since March 23rd. Data from the Met Office regarding weather and humidity suggest that the decrease in NO_x emissions, along with the approximate 10% increase in ozone levels, may have had a profound impact on the air chemistry close to the surface of the earth, affecting humidity. Studies show a direct correlation between SO_2 and relative humidity and, following data for 100 days after the beginning of lockdown, high humidity levels were recorded across the United Kingdom.

High humidity leads to a wet surface reduction, meaning less rain, which directly removes a natural sink for SO_2. This directly correlates to a higher proportion of SO_2 within the atmosphere due to less being held in sinks, accounting for the 100% increase seen during the lockdown period. This, in turn, neutralises the positive health and environmental benefits seen from a reduction of NO_x, since the vast increase in atmospheric SO_2 creates a greater opportunity for acidic rain and its associated negative impact on ecosystems and human health (*3, 4*).

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ECG Early Careers Environmental Brief No. 10 ECGECEB No. 10

Single use plastic pandemic: the rise in disposable plastic pollution during the COVID-19 pandemic

Rebecca Kent (BSc Environmental Science student, University of Reading)

Since the start of the COVID-19 pandemic, the use of disposable plastic products has soared. Previous bans that prohibited their use have been lifted, and many personal protective equipment (PPE) products, including masks and gloves, have also been produced *en masse*, most of which are single use and non-biodegradable. Together, these effects compound the already considerable worldwide plastic pollution issue.

Reasons for single-use plastic increases

Reducing viral transmission PPE has been mass-produced to slow transmission, *e.g.* masks that protect the wearer and others from inhaling droplets which may contain microbes (*1*).

Legal obligations The public have been legally obliged to wear a face mask in shops and on public transport since the 24th of July in the UK (*2*).

Oil industry collapse During lockdown, the demand for petroleum dropped dramatically worldwide. This reduction meant that recycling plastics became more expensive than the production of virgin plastic and products such as disposable cups, straws, and plastic bags resurfaced (*3*).

Individual choices Lockdown measures have led to an increase in takeaways and home deliveries due to the closure of restaurants and avoidance of supermarkets.

Statistics

In February 2021, China manufactured 12 times the typical number of disposable facemasks, with a total of 166 million produced per day (*4*). Globally, approximately 65 billion gloves and 129 billion facemasks have been used per month. If this usage rate continues, there will be enough waste to cover the surface area of Switzerland in 1 year (*5*).

Local case study

Increase in plastic waste production has put pressure on normal waste management strategies, leading to the use of unsustainable practices such as local burning (which releases dioxins into the environment) and direct discharge into landfills. If just 1% all of facemasks were disposed of incorrectly, this translates to more than 10 million items (*3*), which have littered the streets or entered the ocean. A short cycle through Reading uncovered 15 masks and a collection of other single use plastics, as documented in **Figure 1**.

Disposable facemasks are typically composed of plastics, including polyurethane, polypropylene and polyacrylonitrile. Once in the environment, they can be globally distributed by wind, rivers, and ocean currents. The masks can entangle or be ingested by animals and may eventually be broken down into microplastics (*6*).

There remains ambiguity surrounding the definition of microplastics, but they are generally agreed to be

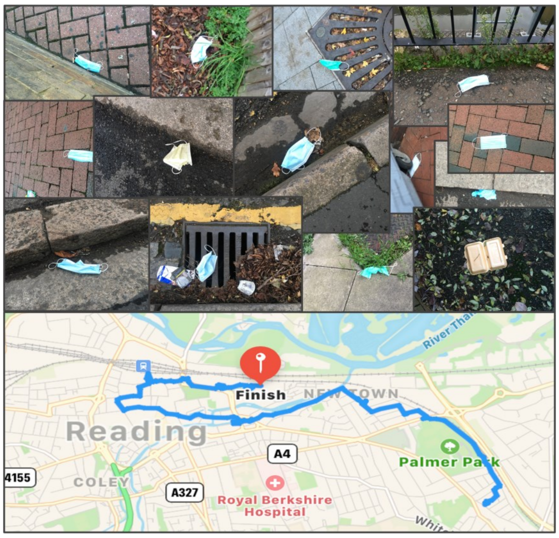

Figure 1. Photos of single use plastic found along a six km route in Reading on 13th November 2020.

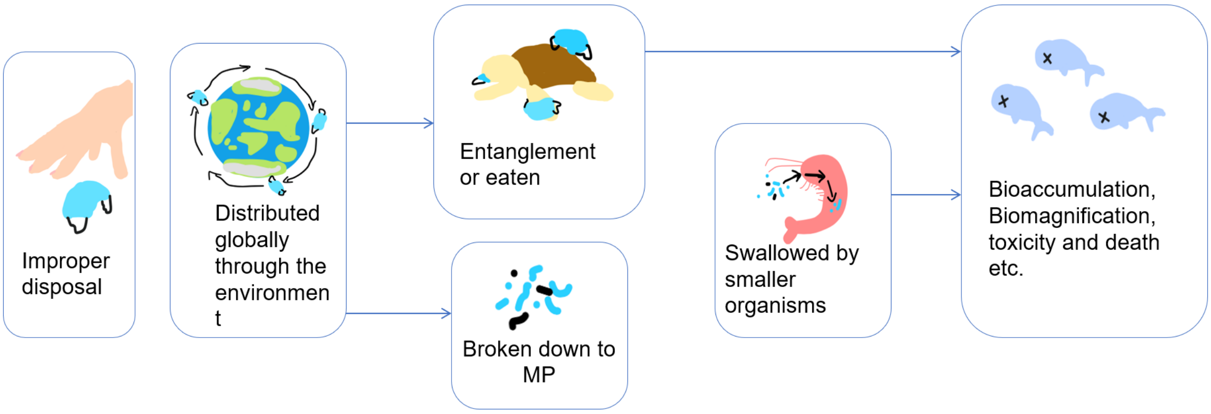

Figure 2. The movement of disposable facemasks through the environment and their impact on wildlife.

< 5 mm (*7*). Once ingested, they can cause internal physiological damage by blocking the digestive tract and organs, increase satiety and thus reduce ingestion and nutrition and, in some cases, cause death. Microplastics are known to have elevated mortality in freshwater fleas after ingestion (*8*). In addition, if ingested by mesopelagic fish species such as the Lantern fish, microplastics increase the fish's buoyancy and prevent them from returning to deep waters, ultimately resulting in mortality (*7*). Not only do microplastics affect individual organisms, but they also bioaccumulate in food chains, negatively impacting species at all tropic levels. Microplastics have been observed continually accumulating in 66% of marine mammals and 100% of sea turtles (*7*), where they may act as a sink for persistent organic pollutants (POPs) such as polybutylene and terephthalate (PBT). Once ingested, lipid-soluble PBT leaches down the concentration gradient, into the tissues of consuming organisms where it is able to enter the food chain and bioaccumulate (*9*). Unfortunately, plastics are highly persistent in the environment, and we are likely to see PPE pollution from the coronavirus pandemic remaining for subsequent decades (*5*).

> **Microplastics are known to have elevated mortality in freshwater fleas after ingestion.**

Solutions/alternatives

Proper disposal Masks should be sealed in plastic bags and put in the general waste bin. The public should be made aware of the consequences of not doing so, as explained in the examples listed above (*5*). Cutting off the ear straps on face masks before disposal prevents entanglement.

Reusable/homemade masks Present environmental benefits, but may be less effective at reducing viral transmission and may compound the pollution associated with fast fashion (*1*).

Conclusions

The COVID-19 pandemic has caused an increase of plastics in the environment, which have resulted in the negative impacts discussed. While there are some measures in place to mitigate these issues, ultimately, it is likely that only after the world recovers will we be able to focus on reversing environmental damage.

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ECG Environmental Brief No. 27 **ECGEB No. 27**

Microbially-enhanced bioremediation of organic contaminants

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Petroleum contamination is the most persistent environmental threat resulting from oil and gas operation. The slow rate of natural attenuation necessitates the development of enhanced remediation approaches. One strategy is the use of bacterial consortia with the environmental adaptability and metabolic capacity for hydrocarbon degradation. In this Environmental Brief, we examine the rational for this strategy and potential biotechnological applications.

Environmental contamination by petroleum and its products is the most persistent environmental menace resulting from oil and gas operations. Spills have occurred in terrestrial and aquatic environments as a result of human error, corrosion and equipment failure (*1*). This has become a major threat to human and animal lives and the environment because of the toxicity of petroleum hydrocarbons (*2*). Consequently, there is an urgent need for effective remediation.

Bioremediation options

Because of the diversity of petroleum contaminants, a number of different remediation options have been investigated. These are classified into two major groups namely, *ex situ* and *in situ*. *Ex situ* techniques involve the excavation and relocation of contaminants for off-site treatments (*3*). As a result, *ex situ* techniques are very expensive and environmentally unfriendly. In contrast, *in situ* remediation involves the on-site treatment of contaminants, and *in situ* methods are both eco-friendly and cost-effective. The United States Environmental Protection Agency (US EPA) indicated that implementing *in situ* remediation of petroleum contaminated sites will result in cost savings of 50 to 80% over traditional methods such as excavation and landfill incineration (*4*).

An *in situ* method that has proved relatively effective for hydrocarbon remediation is phytoremediation, which is the use of plants to clean up contaminated sites. This technique relies on the use of plant interactions (physical, biochemical, biological, chemical, and microbiological) in polluted sites to mitigate the toxic effects of pollutants (*5*). This technique has advantages in that carefully selected plants with fibrous roots serve as a natural host for hydrocarbon-degrading microorganisms. At the same time, extensive rooting systems make it possible for air to penetrate the rhizosphere, thus serving as natural bioventing system, leading to increased biodegradation of pollutants. Notwithstanding the merits of this technique, its longer remediation time, slow growth rate, and slow metabolic activity limit its application. To address this shortfall, there is increasing interest in the isolation of different microbial consortia for enhanced remediation of environmental contaminants. This approach, known as microbially-enhanced bioremediation, offers great potential for effective reclamation of hydrocarbon contaminated sites.

Microbial-enhanced bioremediation

Bioremediation of petroleum hydrocarbons relies primarily on biodegradation by microorganisms through a series of complex processes. Recent studies have shown that the inoculation of petroleum-contaminated soils with hydrocarbon-degrading bacterial consortia or isolates, a technique known as bioaugmentation, can enhance the effectiveness of bioremediation (*6*). The consortia can be used as a stand-alone inoculum, or in synergism with plants (**Figure 1**).

In addition, some of the inoculated microbes enhance the growth of host plants through processes such as nitrogen fixation, and phosphate and potassium solubilisation.

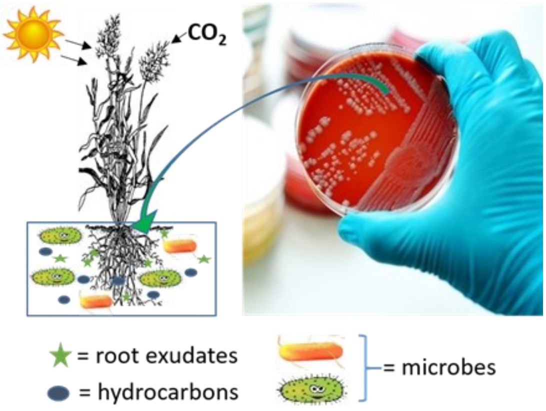

Figure 1. Microbial-enhanced rhizomediation.

In turn, the root exudates released by the host plants provide nutrition to the associated bacteria, enabling continuous biodegradation of contaminants by the rhizobacteria. This synergistic relationship has been described as the ecological driver of rhizoremediation (*7*). As such, it is important to identify novel microbes that can serve as inocula for enhanced bioremediation of organics.

Microorganisms present in contaminated environments hold the key to unlocking most of the challenges associated with bioremediation since they possess both the environmental adaptability and metabolic capacity for contaminant degradation (*8*). These organisms can be isolated from the contaminated environment through successive enrichments using the contaminant of interest as the sole carbon and energy source. This is followed by metagenome functional analysis of the isolated consortium to enable the assessment of its potential to activate and carry out complex processes involved in the degradation of organic contaminants. In aerobic degradation of hydrocarbons, oxygen is both the terminal electron acceptor and a necessary reactant for activating hydrocarbons by converting them into oxygenated intermediates (*9*). This process is orchestrated by monooxygenases and dioxygenases that incorporate oxygen atoms, forming alcohols. The central metabolism of aromatic hydrocarbons involves ortho- and meta-cleavage of catechol and alkylcatechols (*9*). Further oxidation results in the formation of oxoadipate and aldehydes, with the former being metabolised via succinyl-CoA and the latter via acetyl-CoA and propanoyl-CoA (*10*). The inoculation of petroleum contaminated soils with microbes having the ability to perform these complex reactions may speed up the biodegradation of organic pollutants. This is a novel technology, with only a few studies carried out so far, and a handful of inocula developed. Nevertheless, the results of these studies have shown that microbially-enhanced bioremediation is a promising technology with many potential biotechnological applications. Therefore, there is a growing need for more research in this direction.

Microorganisms present in contaminated environments hold the key to unlocking most of the challenges associated with bioremediation since they possess the adaptability and metabolic capacity for degradation.

Conclusions

The pollution of the environment by petroleum hydrocarbons poses serious risks, because of the toxicity of these organics. As a remediation strategy, plant-based techniques offer an eco-friendly and cost-effective alternative over traditional methods. However, slow metabolic activity limits their effectiveness. The development of oil-degrading microbial consortia appears to address this shortfall. These consortia are capable of initiating and speeding up the degradative processes. This is a promising technology capable of enhancing rhizoremediation, since rhizoremediation relies on biodegradation of pollutants by root-associated microbes. The biotechnological application of this remediation approach could speed up the reclamation and restoration of contaminated sites.

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ECG Environmental Brief No. 28 **ECGEB No. 28**

Bacteriohopanepolyol lipids reveal past biogeochemical processes

Rachel Schwartz-Narbonne (Sheffield Hallam University, r.schwartz-narbonne@shu.ac.uk)

Global biogeochemical cycles such as the carbon and nitrogen cycles are regulated by microorganisms. Phytoplankton fix carbon dioxide and methanotrophic bacteria oxidise methane to carbon dioxide; ammonia oxidising microbes convert ammonia to nitrites, and anaerobic ammonium oxidising (anammox) bacteria transform ammoniums and nitrites to dinitrogen. Past fluctuations in microbial processing inform more accurate future modelling of the effects of climate change.

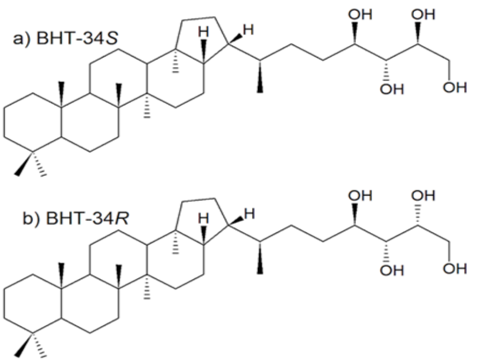

Figure 1. Diastereomers of bacteriohopanetetrol (BHT) include a) BHT-34S and b) BHT-34R.

As bacteria rarely leave fossils, lipid biomarkers such as bacteriohopanepolyols (BHPs) are used to identify their past presence in sedimentary records. BHPs have been used to elucidate the occurrence of marine anammox and peatland methanotrophy (oxidation of methane to carbon dioxide) millions of years ago.

Studying biogeochemical cycles

In the Anthropocene, human activity is drastically changing biogeochemical cycles. Stored carbon is burnt for energy, releasing carbon dioxide, and global nitrogen fixation (the transformation of nonreactive nitrogen gas to reactive nitrogen species such as ammonia) is dominated by the Haber-Bosch process. However, such changes are not unprecedented in geological time. For example, Jurassic and Cretaceous hot-house climates are analogous to today's increased fluxes in greenhouse gases. During these periods, ocean anoxia was widespread, colloquially known as ocean "dead zones", where multicellular life was unable to survive. In order to develop accurate models, therefore, we must go "back to the future" – investigating geological samples.

Studying microbes in ancient biogeochemical cycles presents unique challenges as they do not leave hard-bodied fossils. Whilst there have been considerable improvements in the field of ancient DNA analysis, they have only been applied to samples a few million years old (*1*). In contrast, microbial lipids are preserved for at least 700 million years (*2*), making lipid biomarkers ideally suited to investigate microbial drivers of past carbon and nitrogen cycles.

Bacteriohopanepolyol lipids

BHPs are membrane lipids found in approximately 10% of bacteria, composed of a multi-ring hopane backbone and a functionalised sidechain (**Figure 1**). BHPs have an analogous function to sterols in eukaryotes: they allow bacteria to maintain membrane fluidity during stressful conditions (e.g. extreme temperature) (*3*). While some BHPs, such as bacteriohopanetetrol (BHT-34*S*; **Figure 1a**), are ubiquitous in the environment, others are produced by a limited set of bacteria, making them biomarkers for those species and their environments. For example, two diastereomers of BHT-34*S*, BHT-34*R* (**Figure 1b**) and BHT-*x* are linked to specific bacterial producers which include anammox bacteria and methanotrophs (*4*).

Marine anammox BHPs

Microorganisms drive redox changes in the nitrogen cycle and, before the introduction of the Haber-Bosch process in the early 20th century, were responsible for nearly all nitrogen fixation on Earth. Conversely, microbial activity can also decrease the availability of reactive nitrogen via two anaerobic processes: denitrification and anaerobic ammonium oxidation. *Ca. Scalindua* is the only marine anammox genus and removes ~ 30% of reactive nitrogen, a limiting nutrient to phytoplankton, from the modern ocean (*5, 6*). In the Mediterranean, orbital cycling influences the hydrological cycle, causing periodic eutrophication every 21,000 years. These events appear in sedimentary records as sapropel events. Anammox bacteria produce unique ladderane lipids (**Figure 2**) and they can be traced using the abundance of ladderane lipids in sapropel sediments up to ~125,000 years old (*7*). However, due to their highly strained cyclobutane rings, ladderane lipids do not persist beyond this time (*7*). *Ca. Scalindua* are the only known producer of BHT-*x* (*4*), making it an additional biomarker for marine anammox. BHT-*x* was found in a 2.67 million-year old sapropel sediment, highlighting the role of anammox in Pliocene Mediterranean sapropels (*7*).

Anammox bacteria are also involved in deep ocean carbon fixation, converting inorganic carbon to organic biomass. Recent study of the isotopic signature of BHT-*x* in the Arabian Sea dead zone found that anammox bacteria biomass composed ~ 20% of the organic matter deposited to the sediment (*8*). Anthropogenic climate change and agricultural intensification are projected to enlarge ocean dead zones, with potentially devastating impacts on marine ecology. Anammox bacteria may slow the rate of carbon dioxide increase through carbon fixation and sequestration in dead zones.

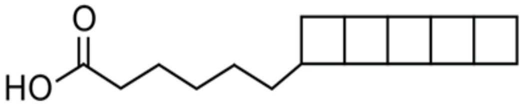

Figure 2 . C_{18}-[5]-ladderane fatty acid structure (7).

Peatland methanotroph BHPs

Peatlands play a key role in the carbon cycle, as they sequester ~ 25% of the world's carbon (*9*). They are also the largest natural source of atmospheric methane, produced by methanogen microbes in anoxic settings. Methane is a potent greenhouse gas: it has over 25 times the global warming potential of carbon dioxide. Methanotrophic bacteria consume methane, reducing emissions. However, climate modellers must understand the effects of environmental changes on methanotrophs. Many terrestrial species produce aminoBHPs such as aminotriol and aminotetrol (**Figure 3**), which are used to distinguish them (*10*). *M. palustris* is an acidic peatland methanotroph proxy, also producing BHT-34*R* (*4*). Abundant aminoBHPs in a well-preserved 56 million-year old peat core, the Cobham Lignite (UK), indicate substantial peatland methanotrophy occurred during this period (*11*). The higher abundance of these methanotroph-derived aminoBHPs in the Cobham Lignite core compared to modern peats may suggest an intensification of methane production and consumption during the Paleocene–Eocene Thermal Maximum, an abrupt global warming event in Earth history (*11*).

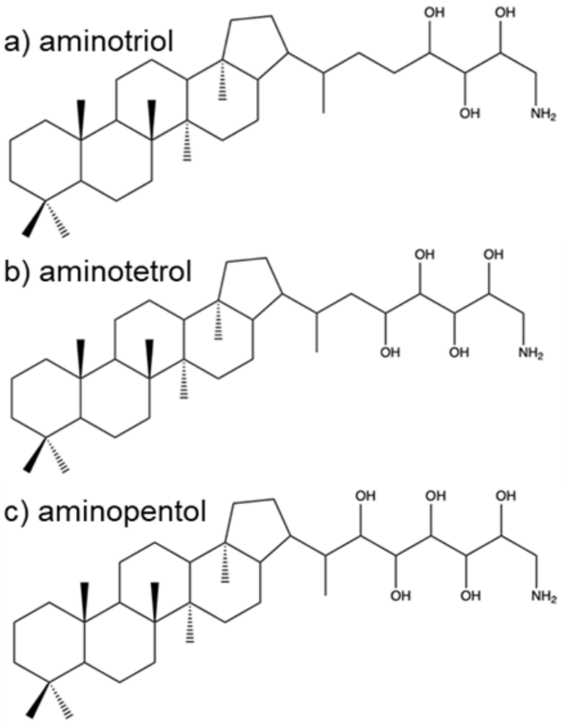

Figure 3. Structures of a) aminotriol, b) aminotetrol and c) aminopentol.

Conclusion

BHP biomarkers have the power to reveal the microbial processes underlying biogeochemical cycles, both in modern times and through geological history, aiding in modelling the present and the future.

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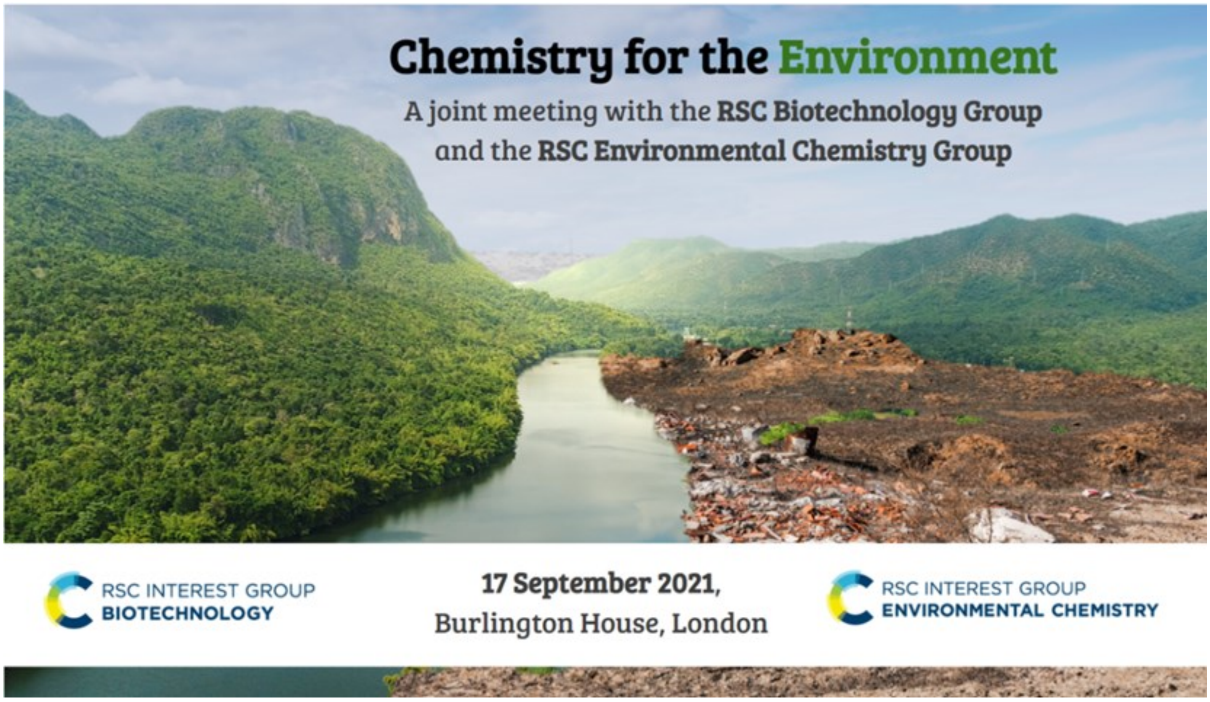
Forthcoming meeting

Chemistry for the Environment

A one-day meeting with the RSC Biotechnology Group and the RSC Environmental Chemistry Group.

Where: The Royal Society of Chemistry, Burlington House, London, W1J 0BA
When: 17th September 2021



Synopsis

The next ten years may hold our last chance to reverse the highly damaging effects industrialised societies have had on the environment. It will certainly be the most important decade in history in terms of the impact our decisions will have on both our environment and societies. The expectation is that scientists will find these solutions, but the challenges go far beyond scaling up research. The next generation of scientists will need to break out of the lab and confidently address the related issues of policy, funding and public engagement.

To address this, the Biotechnology and Environmental Chemistry special interest groups of the Royal Society of Chemistry are organising a unique event for scientists who want to do more for the environment. Our hope for the day is to leave you energised with a new network of like-minded scientists and a greater understanding of what is required from funders and policy makers to maximise impact.

Keynote Speakers

Our speakers include:

Professor Colin Snape FRSE (carbon capture)
Professor Bhaskar Sen Gupta OBE (metal pollution)
Miriam Ribul (circular economy)
Professor Peter Styring FRSC (carbon capture)
Professor Christopher M. Rayner (carbon capture)
Professor Karen Hudson-Edwards (metal pollution)
Professor John McGeehan FRSB FRSC (circular economy)

Full details and biographies for our speakers are available at: http://www.envchemgroup.com/Chem4Env.html

Forthcoming meeting

Disposable attitude: Electronics in the environment

A one-day conference organised by the Environmental Chemistry Group exploring the environmental implications and defences, material scarcity and modern attitude associated with electronics manufacture and disposal.

Where: The Royal Society of Chemistry, Burlington House, London, W1J 0BA
When: Thursday 10th March 2022

The ECG Distinguished Guest Lecture (DGL) and Symposium is our annual flagship event, and focuses on a specific contemporary environmental chemistry topic. Previous DGLs have included antimicrobial resistance, fuel emissions, and nanomaterials. The Distinguished Guest Lecturer is a scientist who is recognised to have made a significant contribution to the field, and is awarded a medal.

Speakers

Professor Ian Williams (University of Southampton)

Ian Williams is a Professor of Applied Environmental Science and Associate Dean within Engineering and Physical Sciences at the University of Southampton. He has an established track record in the field of environmental pollution and waste management.
Professor Williams will speak on the recovery and recycling of materials used in electronics.

Professor Tim Cooper (Nottingham Trent University)

Professor Tim Cooper is leading research in the fields of sustainable design and sustainable consumption, he is Head of the Sustainable Consumption and Clothing Sustainability research groups and a member of the Product Design academic team.
Professor Cooper will speak on sustainable design, sustainable consumption and product life-spans.

Ms Janet Gunter (Restart Project)

Ms. Gunter is an American/British activist, anthropologist who has lived and worked in Brazil, East Timor, Portugal and Mozambique. She has lived in Brixton, south London, for 10 years and feels at home there. She is one of the founders of the Restart Project, a London-based charity established to combat the "throwaway consumerist model of electronics" that has established in the 21st century.
Ms. Gunter will speak on the disposable attitude associated with modern electronics and alternatives to recycling.

2022 Distinguished Guest Lecturer: Mr Steve Cottle (Edwards EMS Ltd)

Mr Cottle is a Senior Applications Manager at Edwards Vacuum. During his 25-year tenure at Edwards, he has worked in multiple technical roles leading advanced development of customer specific solutions for Exhaust Management. He is an industry recognised expert in exhaust management and knowledgeable in all technical aspects of exhaust management. He holds a BSc in Chemistry from Bristol University.
Mr Cottle will speak on the management and pollution of exhaust gases associated with the manufacture of electronics.

Registration

To register, visit the RSC events pages and search for "Disposable Attitude: Electronics in the Environment".

Early Bird Members: £40 (free to join as an RSC member)
Early Bird Non-members: £55
Members: £50 (free to join as an RSC member)
Non-members: £70

EARLY BIRD is available before **1st February 2022**.