

July 2016

ECG *Bulletin*



Promise and perils of geoengineering. Following the 2016 Distinguished Guest Lecture and Symposium, we publish a meeting report (pp. 9–10) and four articles (pp. 11–21) on the science and politics of geoengineering. DGL lecturer Dr. Alan Robock (pp. 19–21) highlights the risks of a widely discussed geoengineering strategy, stratospheric aerosol injection, and concludes that geoengineering must not be seen as a panacea to global warming.

Environmental Briefs. We continue our series with Briefs on waste classification (James Lymer, pp. 23–24) and

the relative-rate technique for calculating rate constants (Martin King, pp. 25–26).

Also in this issue. ECG member Rowena Fletcher-Wood talks about her career in science communication (p. 3), Martin King has fun with a chemistry kit (p. 4), Julia Fahrenkamp-Uppenbrink provides an update on the links between energy and air pollution (p. 5), Tom Sizmur reviews a book on the main elements associated with environmental pollution (p. 6), and William Bloss writes about Criegee Intermediates in atmospheric chemistry (p. 7).

Contents

The ECG Interview: Rowena Fletcher-Wood	3
Product review: Real chemistry for kids, by <i>Martin King</i>	4
Update: Toward a world with cleaner air, by <i>Julia Fahrenkamp-Uppenbrink</i>	5
Book review: Understanding environmental pollution, element by element, by <i>Tom Sizmur</i>	6
Article: Criegee Intermediates: New atmospheric oxidants from old chemistry?, by <i>William J. Bloss</i>	7
Meeting report: Geoengineering the climate: 2016 Distinguished Guest Lecture and Symposium, by <i>Jamie Harrower</i>	9
Article: An introduction to geoengineering, by <i>Joanna Haigh</i>	11
Article: Climate engineering — carbon capture and storage, by <i>Michael Stephenson</i>	14
Article: How can geoengineering research be regulated?, by <i>David Santillo</i> and <i>Paul Johnston</i>	16
2016 DGL Article: Smoke and mirrors are not the solution to global warming, by <i>Alan Robock</i>	19
Forthcoming meetings organized by the ECG	22
ECG Environmental Brief No 12: Waste classification, by <i>James Lymer</i>	23
ECG Environmental Brief No 13: The relative-rate technique for determining rate constants, by <i>Martin King</i>	25



Cover image: The Sleipner oil field, where carbon capture and storage has been in operation for about 20 years. Credit: Kjetil Alsvik, Statoil ASA

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

Executive Editor

Julia Fahrenkamp-Uppenbrink

ecgbulletin@hotmail.co.uk

Production Editors

Rowena Fletcher-Wood, Science Oxford

rowena.fletcher-wood@scienceoxford.com

Tom Sizmur, University of Reading

t.sizmur@reading.ac.uk

Editorial Board

Bill Bloss, University of Birmingham

Zoë Fleming, University of Leicester

Ian Forber, Scientific Analysis Laboratories

Brian Graham, National House Building Council, Milton Keynes

Martin King, Royal Holloway, University of London

Steve Leharne, Greenwich University

Rupert Purchase, Haywards Heath

Roger Reeve, University of Sunderland

Jamie Harrower, INEOS

Environmental Chemistry Group

www.rsc.org/ecg, Twitter: @RSC_ECG,

Facebook: RSCEnvironmentalChemistryGroup

Chair: Zoë Fleming, University of Leicester

(zf5@leicester.ac.uk)

Vice-Chair: Martin King, Royal Holloway, University of

London (m.king@es.rhul.ac.uk)

Honorary Secretary: Tom Sizmur, University of Reading

(t.sizmur@reading.ac.uk)

Honorary Treasurer: Ian Forber, Scientific Analysis

Laboratories (ianforber@yahoo.co.uk)

This and previous issues of the ECG *Bulletin* are available without charge at www.rsc.org/ecg. For ECG membership details, visit www.rsc.org/MembershipECG
Bulletin © The Royal Society of Chemistry – Environmental Chemistry Group 2016
Registered Charity Number 207890

The ECG *Bulletin* is printed on paper made from wood pulp sourced from sustainable forests, and is suitable for archival storage. This issue of the ECG Bulletin was printed by Prismatic Print Solutions, www.prismatic.co.uk; 01444 239000.

The ECG Interview: Rowena Fletcher-Wood

ECG committee member Dr Rowena Fletcher-Wood is a science communicator. Her work includes organising adult science events for Science Oxford, freelance science writing, and tutoring.

What inspired you to become a science communicator?

As a child, I loved drama and acting. Back then, I thought I was more interested in the arts, but a fantastic chemistry teacher inspired me to study chemistry. Not long before I started my PhD in environmental chemistry I realised that I wanted to talk and write about science more than I wanted to research it. So I explored and found a role that combined the two: science communication.

How did you become a science communicator?

Gradually—and through determination. Science communication is difficult to get into because there are few jobs, particularly for recent graduates. Nevertheless, a huge range of science communication roles exist, from administrative roles at the RSC to children's BBC presenters. Only a few places employ teams of science communicators (Science Oxford is one; science museums are others), so for most it is a lonely job. I got into it by multitasking in volunteer roles and taking up training opportunities during my years at university. I became a STEM ambassador and did science communication as a hobby.

Could you describe your current job?

I work three days a week for Science Oxford, where I plan, organise and deliver events that might involve making slime with adults, serious debates on topical scientific issues, or tasting evenings. During the other two days, I write and edit science articles for the science education company Things We Don't Know and write for other organisations, such as Chemistry World, the Diamond Light Source, and companies producing educational resources. I also work as a tutor. Sometimes I perform science stories, magic, or demonstrations in shows. Every week is different, which is how I like it.

What is your advice for anyone considering a career in this area?

Don't give up. Take every opportunity, including things you may not enjoy. Select short-term commitments so that you can find the most productive opportunities. Know your specialties and use them. Don't take unpaid internships, which take work from professionals and are rarely the leg up they claim to be (professional

bodies like the RSC pay their interns). Find someone to help you do your first tax return, even if it is HMRC (they are really helpful when they finally pick up the phone). Network like crazy, join the PSCI-COMM and BIG mailing lists, and go to conferences whenever you can.

What are some of the challenges of communicating science?

Challenges include access to journals, widening participation and reaching the unengaged. Science policy and understanding scientific uncertainty in political decision-making are also really important. My daily challenges include communicating to mixed audiences, getting people to turn up for free events that they have booked, and limiting workshop materials to amounts I can carry.

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

Giving something to people: inspiration, cool facts, or access to knowledge that they could not understand before. I love coming up with creative ideas that make science fun and sharing the science I spent so many years learning.

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

I would be a writer and a climbing instructor. I have written fiction all my life and still do it. I'm also qualified climbing instructor.



Product review

Real chemistry for kids

Martin King (Royal Holloway, University of London, m.king@rhul.ac.uk)

A modern take on the classic chemistry kit is fun yet also pedagogically valuable, according to ECG member Martin King, who tested the kit with his children.

Using a Mel Chemistry Kit, I have had the opportunity to teach my children a little chemistry by stealth and show them the sort of thing that I do all day long. The kit consists of a series of experiment sets that come by post. Combined with a starter kit, the experiment sets allow some simple, elegant experiments to be conducted at home that are interesting, fun, and pedagogically valuable. The sets came with everything we needed, from gloves and glassware to chemicals in little squeezable bottles. The instructions are mainly visual and are supplemented by a wealth of online chemical information about the experiments. The experiments are thus very accessible at two levels: the “fun” level, where one can see chemistry in action, and the detailed chemistry online. Let me be clear about “fun” though—these are proper experiments that are useful, accessible, and rich in chemical principles. We did not make goo or some silly sodium bicarbonate acid volcano for entertainment, with the chemistry glossed over. These are (very) enjoyable chemical education experiments.

The experiment sets are packaged beautifully, and thought has been given to making the experiments easy to conduct. Little things stand out, such as spare chemicals to repeat the experiment, a second set of gloves for adults, and the use of different shapes to avoid confusion when an experiment requires use of two different types of paper. There is even a paper clip (present) to help open the safety catch on the bottles. I was impressed to see that there were even instructions for safe disposal.

In the first experiment, my eight-year-old son and I made batteries that function like AA batteries (see the photo).

We combined the constituent chemicals, packaged them into tubes, placed the tubes in the electrodes, popped the completed batteries into a standard battery holder, and powered different LEDs. The only minor missing instruction was the one telling you which electrical wire to attach to which leg of the diode—but like true scientists, we figured it out by trying different combinations.

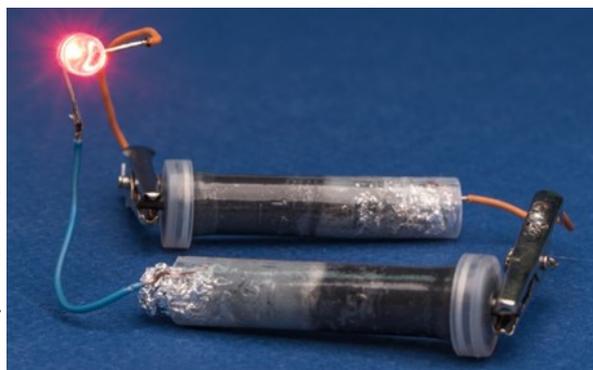
Not to be left out, my eleven-year-old son joined me for a second chemistry session. There were three experiments

in the set, using potassium permanganate, iodine, and sodium disulphite. We investigated the diffusion of iodine into plastic, oxidised the ink from a biro to make it disappear, and reduced purple iodine splodges to iodide. The oxidation of the biro ink was particularly fun, involving mixing of chemicals that dissolve and change colour. While waiting for the oxidation, my son turned to me and said “What, exactly, is going

on?” He wanted to know the science and was genuinely interested in my answer.

The experiments are aimed at children aged 12 or older, but my younger test subjects had fun and I wish I had had a kit like this at their age. There are magnifying glasses for cell phones and glassware for other experiments. There is also a viewer for a smart phone to visualise the chemicals. The latter was curious, as I think my children preferred the chemicals to visualisation. My only criticism from trying these two experiments was that the plastic tray provided could be a bit bigger to catch spillages. I borrowed this kit from a friend, so I have not tried more experiments, but I want to. The kit is designed for home schooling chemistry, but for anyone who can afford it and wants to awaken an interest in chemistry in their children this is a very good place to start.

The Mel Chemistry Kit is available for purchase from <http://melscience.com/en>.



*Home made zinc-carbon batteries.
Image credit: Mel Science*

Update

Toward a world with cleaner air

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

Air pollution causes ~6.5 million deaths annually, according to the World Health Organisation (WHO). The main source of air pollution is fossil fuel and biomass combustion. An International Energy Agency report presents a Clean Air Scenario for reducing deaths from air pollution through tackling energy poverty, reducing pollutant emissions from combustion, and avoiding emissions by promoting clean forms of energy.

The main pollutants considered in the report are sulphur dioxide (SO₂), nitrogen oxides (NO_x), and fine particulate matter (PM_{2.5}, with particle diameters below 2.5 μm). These pollutants mainly derive from the energy sector and are, for example, linked to lung cancer, low birth weight, reduced lung function and heart diseases. Children and the elderly are most vulnerable. In the developed world, most air-pollution-related premature deaths are caused by outdoor air pollution. However, globally, household air pollution is an even bigger problem. The WHO has concluded that half of the almost 1 million global deaths of children under 5 years from pneumonia are a result of household air pollution.

The report considers two scenarios. The New Policies Scenario takes into account current and planned measures to reduce air pollution. This scenario also includes the Intended Nationally Determined Contributions (INDCs) pledged by countries around the world as part of the Paris Agreement. These pledges, if implemented, will increase the proportion of clean energy sources such as wind and solar energy, thereby helping to avoid air pollution. By 2040, SO₂, NO_x and PM_{2.5} emissions will fall by 20%, 10% and 7%, respectively relative to 2015. Yet, deaths from outdoor air pollution will rise overall as urbanisation increases and as populations age, thus becoming more vulnerable to air pollution. Inefficient cook stoves also continue to be used widely, particularly in Sub-Saharan Africa.

The Clean Air Scenario includes additional policies to improve air quality. It focuses on measures that can be implemented without requiring technological breakthroughs. Such measures include strict emission standards in the power sector and for vehicles that have been implemented successfully to reduce air pollution in the U.S., Europe and Japan. The scenario assumes a faster transition away from fossil fuels, as well as universal access to modern cooking fuels and electricity by 2040. Overall, this means that by 2040, emissions will fall over 50% for SO₂ and NO_x and by almost 75% for PM_{2.5}.

Chapters on different countries or regions provide useful case studies for understanding the challenges and implications of the two scenarios. For example, 2.2 million of the current annual deaths from air pollution occur in China, where life expectancy is reduced by 25 months by poor air quality. The New Policies Scenario would increase life expectancy, but nevertheless, almost 2.5 million people are expected to die prematurely in China due to air pollution by 2040. Under the Clean Air Scenario, premature deaths in China are projected to stabilise at today's level by 2040.

Half of the almost 1 million global deaths of children under 5 years from pneumonia are a result of household air pollution.

The report focuses on premature deaths from air pollution, but air pollution also affects people's quality of life in ways not directly linked to survival. Several assessments have concluded that the benefits from air quality improvements far outweigh the costs. Why, then, is progress often slow? One problem is that the mitigation costs are immediate and concentrated, whereas the benefits occur over time periods of decades. Also, many of the benefits cannot easily be measured in economic terms. Nevertheless, there are signs that at least for SO₂ and NO_x, emerging and developing countries are on lower per-capita emissions pathways than those seen in Europe and North America in the past. If the ambitious air quality goals and strategies outlined in the report are accompanied by effective monitoring, evaluation, and enforcement the improvement in life expectancy and quality of life could be substantial.

Energy and air pollution. World Energy Outlook Special Report, OECD/IEA, 2016. Available to download free of charge from www.worldenergyoutlook.org/airpollution

Book Review

Understanding environmental pollution, element by element

Tom Sizmur (University of Reading, t.sizmur@reading.ac.uk)

Human activities disrupt the biogeochemical cycles of many elements on our planet. For example, overuse of nitrogen fertilisers on farmland has caused nitrate levels in rivers to rise sharply. Mercury emissions from fossil fuel combustion, gold mining, and industrial processes contaminate animal tissues in remote Arctic ecosystems. And leaded petrol use has raised lead concentrations in urban soils. In *The Elements of Environmental Pollution*, John Rieuwerts explores the main elements associated with pollution.

The examples above illustrate that the major sources of pollutant emissions to the environment are activities embedded in our 21st century civilisation. As Rieuwerts explains in the opening chapter, it is the behaviour of elements in the environment rather than their presence *per se* that determines whether they cause pollution. Indeed, he closes the book with examples of elements

emitted into the environment that do not cause environmental pollution due to their low reactivity, bioavailability, or solubility (antimony, barium, beryllium, bismuth, cobalt, and tellurium).

Each chapter discusses a particular element, describing how the chemistry of the element in question affects its behaviour in the environment, outlines why and how it is used by humans, and then presents data explaining its environmental impact. For example, the author demonstrates the toxicity of tributyltin to marine invertebrates with data on the incidence of imposex (the

development of male genitals in females) in gastropods on the Argentinian coastline, where tributyltin is used as an antifouling agent on boats. To illustrate the impact of cadmium on human health, he provides data on the relationship between the cadmium content of rice and the prevalence of itai-itai disease (bone softening) in Japan's Jinzu catchment, upstream of the Kamioka mines that discharged cadmium-contaminated sludge from 1910 to the mid-1940s.

Although inorganic pollutants are the main focus, Rieuwerts also highlights major organic pollutants in the chapter on carbon, citing case studies such as the impact of the Deepwater Horizon oil spill on the Gulf of Mexico ecosystem, and the effects of neonicotinoid insecticides on bees. The chapters on bromine and chlorine also emphasise the emissions and impacts of fluorinated flame retardants. Rieuwerts ends by highlighting how little we know about the impacts of rare earth and platinum group elements on the environment, despite their rapidly expanding use by the electronics industry.

The simple, fluent writing style makes this an extremely accessible book, especially for readers without a firm background in chemistry. Complex concepts are explained clearly, with additional background information

provided for non-specialists. For example, a concise diversion into the fundamental concepts of radioactivity provides the reader with just the right amount of information to understand the rest of the chapter on uranium. I would recommend the book to undergraduate and Masters of Science students in areas including environmental science, geography, and environmental management.

The Elements of Environmental Pollution, John Rieuwerts, Routledge, Abingdon, 2015, pp. 331, ISBN: 978-0-415-85920-2



Human activities cause environmental pollution by many elements. Credit: [drpnncptak/Shutterstock](#)

Article

Criegee Intermediates: New atmospheric oxidants from old chemistry?

William J. Bloss (University of Birmingham, w.j.bloss@bham.ac.uk)

Atmospheric composition is affected by reaction with oxidant gases, mainly the hydroxyl radical (OH), the nitrate radical (NO₃) and ozone (O₃). These reactions initiate removal of reactive trace gases, including volatile organic compounds and some inorganic species such as sulphur dioxide (SO₂). Until recently, only OH was thought to react directly with gas-phase SO₂. This changed with the realisation that Criegee Intermediates (CIs) can react at rates relevant for atmospheric chemistry.

Atmospheric SO₂ is the precursor to sulphate in aerosol particles. In addition to being harmful to human health (SO₂ and sulphate aerosols were major components of the London “pea souper” smogs in the 1950s), sulphuric acid supports the formation of new particles, which affect climate by scattering solar radiation and affecting cloud droplet formation. Understanding SO₂ processing is critical for accurate prediction of these effects on the atmosphere.

CIs (zwitterions or biradicals) form in the ozonolysis reaction between O₃ and alkenes (Figure 1). They are named after Rudolf Criegee, who first proposed their existence in 1949 (1). In the gas phase, CIs can act as an additional atmospheric oxidant. Laboratory studies in the 1970s (2) showed that SO₂ oxidation could be enhanced in the presence of alkenes and ozone, providing the first evidence that CIs could react with SO₂. However, accepted wisdom was that reaction with water vapour dominates the removal of CIs in the atmosphere; CIs were thus not considered to be important oxidants.

This picture changed following development of instrumental techniques capable of detecting CIs. Welz *et al.* used photoionisation mass spectrometry to make the first direct observations of individual CI isomers (3). They found that the reaction rates for the simplest CI,

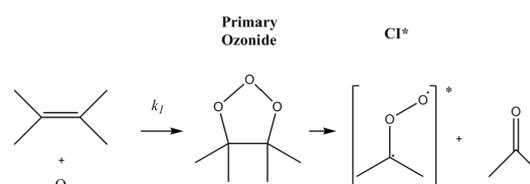


Figure 1. The first steps of the ozonolysis mechanism for 2,3-dimethyl-2-butene lead to formation of the (CH₃)₂CHOO Criegee Intermediate (CI) and acetone.

CH₂OO, with SO₂ were faster than expected by up to three orders of magnitude, whereas the CI + H₂O reaction was comparatively slow. These results implied that CI reactions could contribute substantially to the atmospheric oxidation of SO₂, increasing formation of sulphate aerosol particles. Measurements of sulphuric acid formation in forested regions (where alkene emissions are high) showed that additional oxidants for SO₂, over and above OH, were present (4).

An explosion of research has followed, refining our understanding of the physical chemistry and atmospheric impact of CIs (5). Current understanding suggests that for the smallest CI, CH₂OO, reaction with the water vapour dimer, (H₂O)₂, dominates atmospheric removal, with limited impacts on SO₂, but larger CI species may contribute substantially to SO₂ oxidation. A recent workshop (6) identified key priorities for future research as the need for further laboratory study of CI reaction rates, the development of new methods for synthesising CIs formed from larger alkenes, and the need for approaches to directly detect CIs in the atmosphere.

References

1. R. Criegee, G. Wenner, *Liebigs Ann. Chem.* **564**, 9 (1949).
2. R. A. Cox, S. A. Penkett, *Nature* **230**, 321 (1971).
3. O. Welz *et al.*, *Science* **335**, 204 (2012).
4. R. L. Mauldin III *et al.*, *Nature* **488**, 193 (2012).
5. C. A. Taatjes, D. E. Shallcross, C. J. Percival, *Phys. Chem. Chem. Phys.* **16**, 1704 (2014).
6. Representation of Criegee Chemistry in Atmospheric Mechanisms, 29 February to 1 March 2016, Birmingham, UK. Supported by the ECG and the NERC [NE/K005448/1]



Invest in your Future

Advance your career as a Chartered Environmentalist (CEnv) and stand out from the crowd!

The Royal Society of Chemistry has recently been licensed to award Chartered Environmentalist (CEnv) on behalf of the Society for the Environment (SocEnv). As a Member (MRSC) or Fellow (FRSC), you can now apply for Chartered Environmentalist (CEnv) status.

The environmental challenges we face mean that the role of the Chartered Environmentalist is more important than ever.

Gaining chartered environmentalist status sets you apart from others working in your field. It demonstrates proven knowledge, experience, dedication and commitment to professional standards.

To find out how you can apply to be a Chartered Environmentalist, go to <http://rsc.li/chartered-status>



Meeting report

Geoengineering the climate

Jamie Harrower (INEOS, jamieharrower@hotmail.com)

This year's Distinguished Guest Lecture and Symposium on Geoengineering the Climate took place on 22 March 2016 at Burlington House, London. Attended by about 100 delegates, the event provided a comprehensive overview of the science and policy challenges of geoengineering.

In her introductory talk, **Professor Joanna Haigh (Imperial College London)** outlined the challenges that humanity faces in combating climate change and summarised the main factors contributing to an increase in the Earth's temperature. Her talk illustrated the increase in the Earth's temperature since 1850, the decrease in Arctic summer sea ice, the rising global average sea level, and the increase in the average ocean heat content. She emphasised that the physics of the greenhouse effect are simple and have been known since the 19th century.

There are few options to tackle climate change on the timescales required to limit the mean global temperature rise to below 2 °C, as stated in the COP 21 agreement in Paris 2015. Exceeding this level of temperature increase may cause dramatic changes in the Earth's weather systems. The options are to adapt to the global impacts of global warming, to significantly reduce greenhouse gases emissions, and/or to use geoengineering. Geoengineering has been defined by the Royal Society as "the deliberate large scale manipulation of the planetary environment to counteract anthropogenic climate change."

Geoengineering schemes can be divided primarily into land-, ocean-, atmosphere- and space-based approaches. Professor Haigh explained that, fundamentally, there are two different methodologies. The first aims to remove carbon dioxide (CO₂) by physical or chemical means (carbon dioxide removal, CDR). The main CDR schemes are large-scale afforestation, biochar production, carbon capture and storage (CCS), and ocean fertilisation. However, CDR schemes can only sequester a small amount of CO₂ compared to anthropogenic emissions and are thus unlikely to prevent the global mean temperature from rising 2 °C by 2100. The second methodology, solar radiation management (SRM), aims to adjust the amount of sunlight reaching the Earth,

thereby counterbalancing greenhouse gas forcing. The main SRM schemes are injecting sulphur into the stratosphere to block UV light, placing sun shields to reflect sunlight, and injecting sea salt into the air above the sea to increase the reflectivity of clouds. SRM can significantly decrease the solar radiation absorbed by the Earth and therefore lower the average temperature globally. However, if SRM is discontinued, temperatures could rise rapidly. SRM also does not address the effects of high atmospheric CO₂ concentrations, such as ocean acidification. The costs and benefits of geoengineering vary across the globe, with some countries gaining significantly, while others may be faced with a worse scenario than prior to geoengineering intervention.

Professor Mike Stephenson (British Geological Survey) next spoke on "Climate geoengineering—carbon capture and storage." He started by explaining how coal layers formed around 300 million years ago when dense forest areas on Earth were buried and protected from oxidation, thus removing carbon from the active carbon cycle. By the 1700s, Britain had started to return this captured carbon back into the atmosphere, having become reliant on coal as an energy source in its expanding cities. According to Stephenson, this marked the start of the Anthropocene, a proposed geological time period in which human activities have fundamentally altered the Earth's geological processes. Today, the use of coal is increasing in parts of the world such as China and India. Globally, there are around 50,000 coal-burning power stations, with about 8,000 based in the U.S.

Professor Stephenson argued that CCS may be one of the few viable options for reducing CO₂ on the timescales required to limit global warming. Established technologies for capturing carbon during energy production mainly involve two steps: CO₂ is first removed from the flue gases after coal has been burnt and then injected into deep geological layers to contain the CO₂ below impermeable rock. Offshore reservoirs may allow storage of ~78 gigatons of carbon. The injection of waste materials into geological formations is not new: the U.S. has over 140,000 disposal wells currently used by the oil and gas industry. However, CCS is not yet widely used. The Sleipner CO₂ storage project in Norway is the most successful to date, having safely stored 20 million tonnes of CO₂ in subsurface sites. The Schwarze Pumpe power station in Germany, a pilot scheme for CCS, has not been in operation since 2014.

Many policy makers see bioenergy and carbon capture storage (BECCS) as a credible option for reducing atmospheric CO₂ concentrations. The idea behind BECCS is to produce negative CO₂ emissions by growing energy crops, burning them for energy, and then capturing the resulting CO₂ for storage. The implementation of a global bioenergy programme will provide numerous benefits; however, suitable carbon storage locations may be physically far from a bioenergy production region. Furthermore, large-scale energy crop production would compete with food production and is likely to have negative environmental implications.

The third talk was delivered by **Dr David Santillo (Greenpeace/University of Exeter)**, titled “How can geoengineering research be regulated?” The speaker focused on recent advances in regulating ocean fertilisation projects. Ocean fertilisation involves adding iron into the ocean environment to stimulate the growth of phytoplankton. This could potentially increase the rate of carbon sequestration and decrease the atmospheric CO₂ concentration. Adding Fe to enhance phytoplankton growth could have positive effects on overfished fish stocks, but it may also have negative effects, such as the development of toxic algae blooms. Field and laboratory studies conducted over the past 15 years have shown that adding Fe to high nitrite and low chlorophyll (HNLC) regions can stimulate phytoplankton blooms, which has led to a better understanding of Fe role in the oceans ecosystems. This has also contributed to the better understanding of links between ocean productivity and the Earth’s climate.

Dr Santillo described the criteria and international guidelines set out in the Ocean Fertilisation Assessment Framework (OFAF), which was designed and implemented by the international marine organisation (IMO) to determine whether proposals for ocean fertilisation constitute legitimate research. Any activities that do not meet the criteria set out in the framework cannot proceed to the next stage of assessment without further revision. Developed over the course of just six years, the Framework shows that regulation of

geoengineering is possible. The Framework may be extended to other ocean-based geoengineering schemes and may also serve as a guide for geoengineering schemes based on the atmosphere or on land.

In his Distinguished Guest Lecture, **Professor Alan Robock of Rutgers University** spoke on “Smoke and mirrors are not the solution to global warming.” He focused on the controversial concept of injecting sulphate aerosol precursors into the stratosphere to deflect sunlight in an effort to counter global warming. As the speaker stressed, notable climate scientists have suggested that geoengineering should only be considered as an emergency response and not a long term solution to climate change.

Professor Robock outlined the risks and benefits from stratospheric geoengineering. The benefits include reducing global surface air temperatures, which could potentially reverse the negative impacts of global warming, and an increase in plant productivity that may increase the terrestrial CO₂ sink. There are, however, many more risks associated with stratospheric geoengineering, which include large-scale drought in Asia and Africa, ozone depletion, continued ocean acidification and potentially rapid global warming if suddenly stopped.

There is also the question of who controls the global thermostat and who stands to benefit or suffer as a result, with the potential for conflict between nations if any one country or group of countries decides to proceed without global agreement.

Professor Robock concluded that mitigation and adaptation to climate change must come first. Albedo (reflectivity of the Earth’s surface) modification should not be used at this time, but should be the subject of laboratory and modeling research. Studying volcanic eruptions will also be important, as these provide natural experiments on the effects of stratospheric sulphur injections. Research into governance and ethics will be crucial to ensure that any field experiments or deployments of SRM are tightly controlled.



Natural experiment. Volcanic eruptions, such as that of Mount Bromo in Indonesia shown here, help to understand the effects of stratospheric geoengineering. Credit: Wan Fahmy Redzuan/Shutterstock

Article

An introduction to geoengineering

Joanna Haigh (Imperial College London, joanna.haigh@ic.ac.uk)

By trapping infrared radiation, naturally occurring greenhouse gases maintain the Earth's average surface temperature at ~33 °C warmer than it would be without an atmosphere. About two-thirds of this warming is due to the presence of water vapour and about one-third to carbon dioxide (CO₂); other gases play much smaller roles. As the concentrations of man-made greenhouse gases (particularly CO₂ and methane) rise, so does the trapping of heat radiation. As a result, the global average surface temperature rises roughly in proportion to the logarithm of the CO₂ concentration. Various schemes have been proposed to control this global warming through geoengineering.

The most obvious means of slowing down or preventing further warming is to reduce emissions of greenhouse gases, and this is the path enshrined in the UNFCCC COP21 accord agreed in Paris in December 2015. This espoused the aim of keeping the world to a warming less than 2 °C above the pre-industrial level, a level which has the potential to cause climate change with severe impacts on human activity and the natural environment. This historic event marked a major step forward in international action on climate change but achieving the required cuts in emissions is a major challenge. Indeed, unless global greenhouse gas emissions are reduced to net zero by the middle of the century, it is likely that this threshold will be crossed. Here, "net zero" implies an understanding that it will not be possible to completely stop greenhouse gas emissions and that some technologies to extract CO₂ from the atmosphere will be necessary.

In the absence of sufficient greenhouse gas emissions reductions, or to buy time to reduce emissions, various schemes have been proposed for large scale intervention in the climate system (Figure 1). These schemes for geoengineering the climate can be divided into two fundamentally different approaches (1, 2).

Carbon dioxide removal

Carbon dioxide removal (CDR) techniques directly remove CO₂ from the atmosphere. In the following list, the first two are examples of the "negative emissions technologies" mentioned above.

Carbon Capture and Sequestration (CCS) at source.

Technologies that can capture up to 90% of the CO₂ emissions produced are introduced into electricity generation and industrial processes. The captured gas is then transported by pipeline or ship and injected into geological rock formations from which it is assessed to be vanishingly unlikely to reemerge.

Sequestration of biomass. Crop waste or charcoal can be buried on land or in the deep ocean. Crops grown for bioenergy and biofuels (although with potential adverse impact on food production) might be utilised with CCS. The potential impacts on ecosystems of all sequestration methods need to be assessed. Methods for sequestration of CO₂ from ocean gas platforms in Utsira formations (layers of sand and brine under the sea floor) have already been designed, and might be implemented for other sources, but the costs are high and longevity and leakiness needs to be better understood.

Land use management, afforestation. Careful planting can help limit the growth of CO₂ concentrations, has few side effects (except possible land use conflicts, demands for water or implications for biodiversity) and could be implemented immediately and cheaply. The scope for significant impact is, however, small.

Enhanced weathering. For this, the reaction of atmospheric CO₂ with silicate minerals (such as olivine) would be accelerated, and the resulting carbon-containing solids would be stored on land or in the ocean. This approach would involve mining, treatment and transportation of the minerals, with significant energy implications. It would also be slow to take effect.

Chemical capture of CO₂ from the air. "Artificial trees" have been designed to extract atmospheric CO₂. The technology appears to be feasible, but again must cope with the problems of scale as well as those associated with CCS.

Enhancement of CO₂ take-up by ocean plankton. This would be achieved by enhancing photosynthesis by

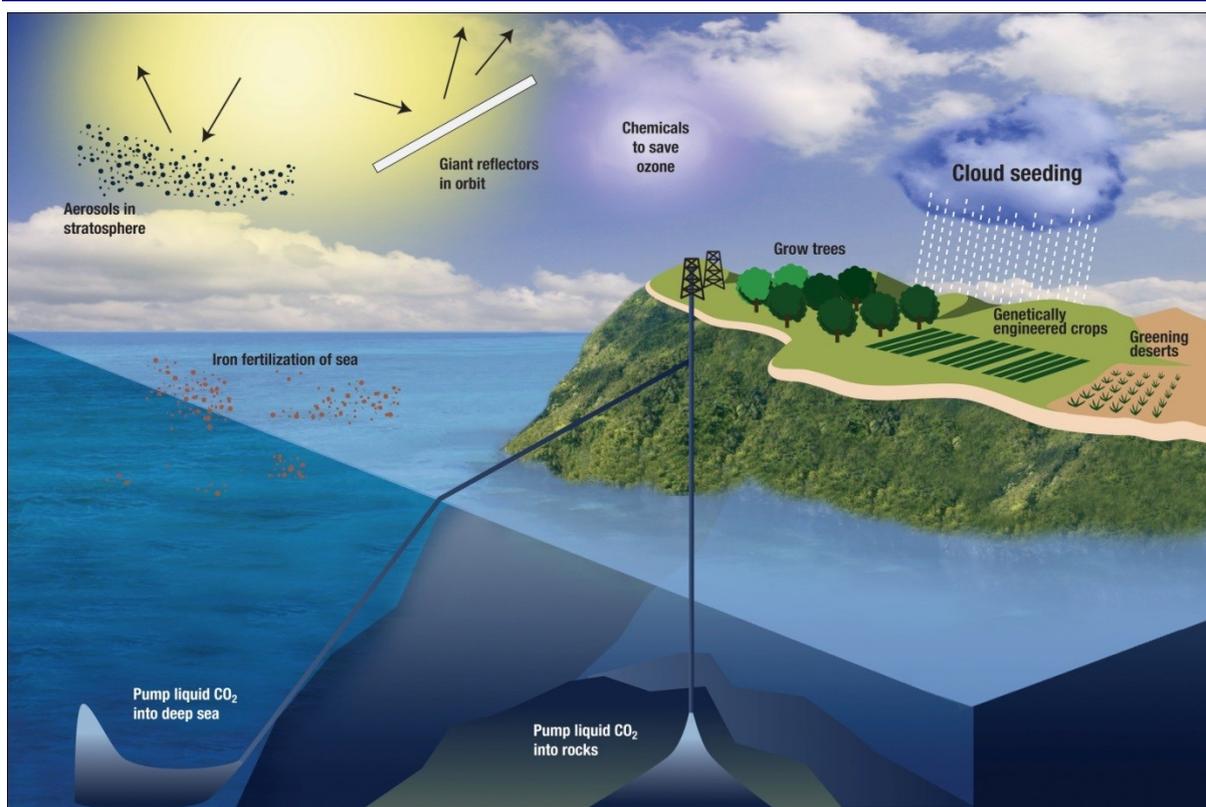


Figure 1. A schematic representation of some geoengineering proposals. Credit: Kathleen Smith/LLNL

increasing the availability of the necessary nutrients – either by “fertilisation” of the ocean with Fe, P or N or by (wind or tidal-driven) pumping of deep ocean water to the surface. There is currently insufficient evidence to determine whether this would be effective and an important consideration must be the potential for undesirable ecological side effects.

Solar radiation management

Solar radiation management (SRM) techniques which reduce the amount of solar energy absorbed by the Earth by enhancing global albedo (reflectivity) and thus returning some solar radiation back to space. These include the following approaches:

Space-based reflectors. Proposed schemes include the launch of trillions of small refracting disks up to the L1 (equal gravity) point between the Earth and the sun or the manufacture on the moon of refractors made from lunar glass.

Stratospheric aerosols. Sulphate particles injected into the stratosphere would simulate the effects of massive volcanic eruptions, which have been shown to introduce temporary reductions in global mean temperature. Of concern here would be indirect effects on stratospheric ozone concentrations and atmospheric acidity.

Enhancement of cloud reflectivity. It is proposed that this might be achieved by the injection of sea salt particles into clouds (or potentially cloudy regions) from specially designed ships. The salt particles would act as condensation nuclei for cloud droplets and the resulting cloud, composed of more numerous but smaller droplets than might otherwise exist, would have higher reflectivity and, probably, longevity.

Enhanced land surface albedo. This might be achieved through the use of more reflective crops, or by covering deserts with highly reflective material, or by painting urban settlements white. These schemes tend to be very expensive and may produce undesirable local ecological impacts.

CDR versus SRM?

CDR techniques might be viewed as preferable to SRM techniques in that they attempt to return the climate to a more natural state and they would, in general, be safer. However, CDR tends to be very slow to take effect and current schemes are very costly if they are to make significant impact (**Figure 2**). Furthermore the methods for the carbon sequestration required as part of most of these schemes are not well-proven to be without undesirable environmental side effects.

SRM techniques are inherently less safe than CDR methods in that, while they provide a correction to the global radiation imbalance introduced by the greenhouse gases, they do not return the atmosphere to its natural state. They do nothing to reduce other effects of high CO₂ concentrations, such as ocean acidification. They also place the climate in an unnatural “High CO₂ Low Sun” state under which atmospheric winds and circulations may be quite different and could result in unforeseen impacts on, for example, regional precipitation patterns. SRM schemes have the advantage of being generally less expensive. They would also be easier than CDR methods to implement (or reverse) swiftly. If, however, they were introduced with a view to long term mitigation of global warming, then humankind would be committed to maintaining them into the indefinite future. Any sudden cessation of the SRM would plunge the world very fast into the much warmer state associated with higher CO₂ concentrations (3).

While the scientific and technical issues posed in the development of geoengineering methods are challenging, possibly an even greater problem would come in addressing ethical and political issues (4). Some schemes, such as capture of CO₂ from the air, might be regulated with existing national legislation such as pertains, for example, to air pollution. Other geoengineering methods, such as space-based reflectors or stratospheric aerosol injection, would have large-scale effects, and some regions of the globe may find (or perceive) these to be of greater benefit. There are no clear mechanisms to govern the implementation, operation or control of geoengineering activities, although international agreements concerning the control of nuclear weapons, or indeed climate change, might be used as models.

Another ethical aspect (“moral hazard”) concerns the possibility that the very existence of geoengineering schemes might discourage concerted action to reduce CO₂ emissions. This is a very serious concern, but I fear

that this has already happened. Hence we find a surge of international interest in geoengineering schemes.

No geoengineering method has been identified that can address the issue of climate change in a timely, safe and affordable way. The problems of international governance may prove insurmountable. It cannot be stated strongly enough that the safest and most reliable way to combat climate change is to attack the problem at source, to identify carbon-free sources of clean energy and manufacturing and, importantly, to use existing energy resources as efficiently as possible.

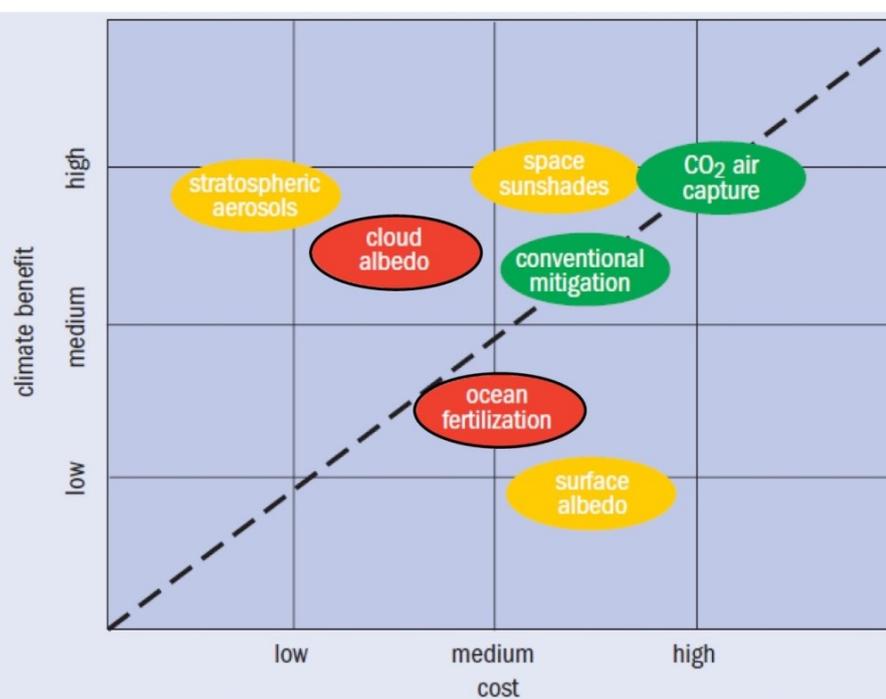


Figure 2. A cost - benefit diagram for geoengineering proposals, along with conventional climate change mitigation. The risks associated with these proposals are indicated as low (green), medium (yellow) and high (red). The safest alternative to conventional mitigation is CO₂ air capture, but stratospheric aerosol injection has the best benefit-to-cost ratio. Reprinted with permission from (4).

References

1. Royal Society, *Geoengineering the climate: Science, governance and uncertainty*. Policy Document 10/09, 2009.
2. National Research Council, *Climate Intervention: 1. Carbon dioxide removal; 2. Reflecting sunlight to cool Earth*, National Academies Press, 2015.
3. A. Robock, this issue, page 19.
4. P. Cox and H. Jeffrey, *Physics World*, September 2009, p. 24.

Article

Climate engineering — carbon capture and storage

Michael Stephenson (British Geological Survey, mhste@bgs.ac.uk)

Carbon capture and storage (CCS) is a technology to reduce the amount of anthropogenic CO₂ in the atmosphere. CCS tends to be associated with fossil fuel power stations, particularly those that burn coal, but could be used on any large point source of CO₂ in power generation or manufacturing, such as ammonia and cement factories and coal-to-liquid plants. The separated CO₂ can then be sequestered (stored) in deep rock layers. More recently, Bioenergy with Carbon Capture and Storage (BECCS) has received attention, but the environmental implications of large-scale biomass burning for energy remain unclear.

Long before Britain generated electricity from coal, it was using this organic-rich mineral in large quantities. Before 1700, fossil fuels had already overtaken wood as the leading provider of heat in peoples' homes. Plentiful coal in the north of England enabled the natural supply of non-fossil energy to be bypassed. So began what the historian Andreas Malm has called the 'fossil economy' (1), which relies on burning carbon that comes not from local growing sources (trees), but from plant sources that are 330 million years old. From 1781, cotton manufacture, previously based near fast-flowing streams, became independent of water when the rotative steam engines of Boulton and Watt led to the growth of large, steam-powered mills concentrated in towns like Manchester and Salford. Steam engines for winding gear and pumps followed and meant that even more coal could be mined. This start of the fossil economy might also be seen as the start of the latest of the geological epochs, the Anthropocene (2), marked geochemically by, amongst others, the rise in CO₂, as recorded in ice cores.

That relationship with coal is weaker in Britain today, as most of our electrical power is now generated by burning



Miscanthus sinensis. This perennial energy crop is one of the main candidates for BECCS. Credit: fuujin/Shutterstock.

gas. But coal continues to be used elsewhere in the world. Predictions, such as those of the International Energy Agency (IEA), suggest that coal will continue to be used heavily in the future, and will probably be important for global electricity generation for many years to come. According to the most recent IEA forecast (3), coal demand will grow to 5814 million tonnes of coal-equivalent per year through 2020, a rate of 0.8% per year on average. Half of the growth will be in India. It is difficult to see India reducing CO₂ emissions without CCS.

The EU has committed to cutting its greenhouse gas emissions to 20% below 1990 levels by 2020, and further cuts are being decided for 2050. This commitment is one of the headline targets of the Europe 2020 growth strategy and is being implemented through binding legislation. Power generation will have to take a particularly large part in emissions reductions, mainly by focussing on increasing surface renewables (wind, tidal and solar), nuclear and geothermal power, but also by reducing emissions from existing fossil fuel power plants, partly by CCS.

CCS has received new interest recently because it may be an important part of achieving the 2 °C limit set at the 2015 United Nations Climate Change Conference, COP 21, concluded in Paris in December 2015. Many of the Intergovernmental Panel on Climate Change (IPCC) climate scenarios include some form of "negative

emissions”—that is, net permanent removal of greenhouse gas emissions from the atmosphere. Of the 400 IPCC climate scenarios that have a 50% or better chance of less than 2 °C warming, more than 300 assume the successful and large-scale uptake of negative-emission technologies.

The most popular of these technologies is Bioenergy with Carbon Capture and Storage (BECCS). The idea behind BECCS is fairly simple: grow energy crops and burn them



The Sleipner oilfield. Carbon capture and storage at this site has been in operation for 20 years. Credit: Kjetil Alsvik, Statoil ASA

in power stations for electricity, scrub out the CO₂ and sequester it permanently in the subsurface. Some commentators see two approaches to staying below 2 °C warming: the ‘pay early’ and ‘pay late’ plans. In the first, countries have to slash greenhouse gas emissions immediately; the second allows a slower phase-out by developing negative emissions, particularly BECCS. To some, BECCS is the last resort in the latter part of the century if all else fails to cut emissions.

One important constraint on BECCS is how much land and resource can be devoted to biofuel crops. In a world where population is growing and land and other resources are at a premium, can space be devoted to crops that we simply burn? Many think not. As noted by Smith and Torn (4), very high sequestration potentials for BECCS have been reported, but there has been no systematic analysis of the potential ecological limits to, and environmental impacts of, implementation at a scale consistent with climate change mitigation. Modern fossil fuel use emits about 8 Pg C y⁻¹ (petagrams of carbon per year). Using a simple model, Smith and Torn estimated that to remove just 1 Pg C y⁻¹ by burning biofuel would require at least 2×10⁸ ha of land (20 times the area

currently used for bioethanol production in the USA), 20% of today’s global fertiliser nitrogen production, and 4×10¹² m³ y⁻¹ of water. No one really knows if this is possible.

The UK Energy Technologies Institute (ETI) has worked intensively on what a British BECCS industry might look like: the crops that might be burned, quantitative models of biomass growth, soil chemistry and greenhouse gas emissions (5). ETI projects and other work suggest that the most attractive biomass feedstocks today are short rotation forestry species (such as Scot’s pine and poplar) and perennial energy crops (miscanthus, see the first photo, and short rotation coppice willow or poplar). The ETI sees BECCS as the “only credible route to significantly reduce atmospheric carbon (negative emissions) – unlocking the ability to meet national carbon targets at a much lower cost” (5).

In contrast to the uncertainties over the environmental sustainability of BECCS, subsurface CO₂ storage is well understood and has been operating successfully in a number of large pilot test sites for several years. For example, every year since 1996, about 1 million tonnes of CO₂ have been stored in a rock layer more than 800 metres below the seabed in the North Sea at Sleipner (see the second photo) (6). It seems likely that CCS on industrial point sources such as coal (and gas) power stations, ammonia and cement factories, and coal-to-liquid plants, will be part of the mix of technologies required to keep CO₂ emissions down.

References

1. Andreas Malm, *Fossil Capital: The Rise of Steampower and the Roots of Global Warming*, Verso, 2016.
2. C. N. Waters *et al.*, *Science* **351**, aad2622 (2016).
3. International Energy Agency, *Medium-term coal market report 2015*, IEA 2015.
4. L. J. Smith, M. S. Torn, *Climatic Change* **118**, 89 (2013).
5. Energy Technologies Institute, *Bioenergy: Enabling UK biomass*, ETI, 2015.
6. See www.statoil.com/en/technologyinnovation/newenergy/co2capturestorage/pages/sleipnervest.aspx.

Article

How can geoengineering research be regulated?

David Santillo (Greenpeace Research Laboratories, d.santillo@exeter.ac.uk) and Paul Johnston (Greenpeace Research Laboratories)

The term climate engineering (or geoengineering) refers to a broad range of concepts, some with a history of practical research, others still largely theoretical. These concepts range from artificially enhanced mineral weathering and large-scale ocean fertilisation to modifying the chemistry of the upper atmosphere or making croplands or seas more reflective. Assessments of their likely effectiveness in mitigating climate change and their potential for adverse effects have highlighted substantial uncertainties and unknowns (1, 2). In 2009, the Royal Society concluded that although “geoengineering of the Earth’s climate is very likely to be technically possible... the technology to do so is barely formed, and there are major uncertainties regarding its effectiveness, costs, and environmental impacts” (3). Seven years on, that assessment remains just as valid.

In response to the limited knowledge and understanding of what might happen in a geoengineered world, some call for an expansion and acceleration of research (4), including stepping beyond modelling studies to the design and conduct of field experiments or even proof of concept engineering trials. By definition, such experiments would need to be carried out at scales sufficient to generate measurable effects that could be distinguished from background variability, and the area (or volume) of impact could neither be precisely defined nor contained. This raises the questions of whether and, if so, how such proposed research could be properly assessed, regulated, controlled and monitored. How

could research at scale be distinguished from actual deployment of a geoengineering technique? And who would bear responsibility for the review and authorisation of such research and would ultimately be liable for any damages or other impacts caused?

Unless studied with theoretical models or in contained laboratory experiments, geoengineering experiments will not respect geographical boundaries. In fact, it is the potential for transboundary impacts, which may be uncontrollable and possibly irreversible, that has led to strong international concerns regarding proposals for field research into geoengineering concepts. For the same reasons, any mechanisms put in place to provide independent oversight and control of such research must also be international in nature, incorporating elements of cautious and consistent assessment and consultation. This may sound like an impossible task in a world in which collective action to tackle climate change itself has been so painfully (and dangerously) slow, but recent efforts to regulate ocean fertilisation studies provide a relevant precedent in international environmental law.

Ocean fertilisation was first proposed as early as the 1960s as a way of boosting fisheries production to feed a growing population. About 15 offshore field experiments have been carried out in the last couple of decades, driven by various hypotheses. These experiments have tended to confirm that adding iron as a nutrient to offshore waters, in which algal populations are lower than expected given the supply of nitrogen and phosphorus, commonly boosts their growth. What happens to the plankton community from there, however, appears far less predictable, not least because the final outcome depends heavily on the starting conditions and on the weather and oceanography as the experiment progresses (5).

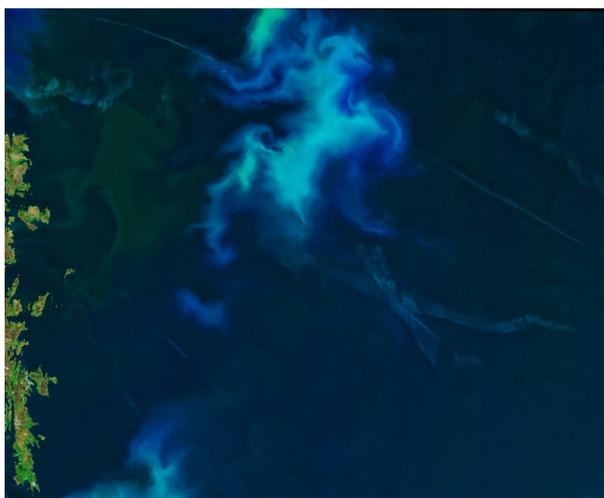
Despite these limitations, promotion of iron fertilisation as a method of stimulating the drawdown of carbon dioxide from the atmosphere became more prominent at the turn of the millennium. From the start, many marine scientists warned about harmful consequences for marine ecosystems (6). It was in 2007, however, that the

proposed actions of a handful of commercially driven companies focused the attention of international regulatory bodies with responsibility for protecting the marine environment. In particular, a high-profile announcement by the company Planktos of its intent to conduct a large-scale iron fertilisation experiment in the South Pacific Ocean (near the Galapagos Islands) and to create and sell carbon credits as a result, led rapidly to the issuance of a statement of concern by the Scientific Groups that advise the Parties to the London Convention and Protocol (LC-LP). These concerns were endorsed at a political level in the same year. By October 2008, the LC-LP Parties had passed a formal resolution to rule that ocean fertilisation activities other than for legitimate scientific research were not allowed (7).

This was something of a departure for the London Convention, a legal instrument established in the 1970s to deal primarily with the dumping of wastes at sea, but was a development that nonetheless recognised the parallel concerns for marine ecosystems that would arise from deliberate attempts to fertilise the oceans. Early in 2009, work began within the LC-LP Scientific Groups to define an assessment framework for ocean fertilisation, defined as “any activity [other than conventional aquaculture] undertaken by humans with the principal intention of stimulating primary productivity in the oceans”. The framework was completed by October 2010. Final adoption of the approach through legally-binding measures followed three years later, and although it is still to enter into legal force globally, all parties to the London Convention and Protocol (more than 90 countries worldwide) have continued to observe the spirit of the original resolution. One uncontrolled iron fertilisation activity, carried out by a private company off the west coast of Canada in 2012 and with no prior independent assessment, remains subject to legal proceedings under Canadian law.

The Ocean Fertilization Assessment Framework (OFAF) (8) sets out how proposals should be assessed by national or regional authorities, including an initial assessment to reject those that are not legitimate scientific research, i.e. those for which the scientific

purpose or objectives are weak, there are no commitments to transparency, publication and peer review, or there are concerns that economic interests might drive or bias outcomes. Thereafter, the OFAF is technical in nature, and aims to establish and assess the scale of risks to the marine environment. This approach to regulation does not, therefore, prohibit research, but does place reasonable limits on when, where and how it might be carried out and for what purpose.



Natural phytoplankton bloom in the North Atlantic. Ocean fertilisation aims to create artificial blooms to draw carbon dioxide out of the atmosphere. NASA Earth Observatory image by Joshua Stevens, using Landsat data from the U.S. Geological Survey.

Although the focus has so far been on ocean fertilisation because of the perceived immediacy of the threat, amendments to the legal text of the London Protocol are designed to address concerns arising from other marine geoengineering activities that might develop as practical realities in the future. Such activities include alkalinity management, enhanced upwelling, and reflectance management using microbubbles or foams. Although each proposed activity may require some unique elements of assessment

and control, the general principles of (i) governance before research, (ii) allowing only activities determined to be legitimate scientific research, and (iii) setting standards and expectations for peer review and prior consultation apply to all. The legal framework is, in effect, ready to be adapted for the future (9).

The LC-LP approach cannot, of course, directly address geoengineering activities proposed beyond the marine environment, i.e. on land or in the atmosphere above land or sea. Atmospheric geoengineering encompasses an equally diverse array of concepts, ranging from the modification of clouds in the lower atmosphere to the release of sulphates, alumina, titanium dioxide and even dust into the upper atmosphere in attempts to reduce incoming solar radiation. Such interventions would arguably be even more difficult to contain and control than those in the sea. Scientists have raised serious concerns about uneven distribution of impacts on temperature and weather patterns and disruption of rainfall, among others (10).

When ocean fertilisation emerged as a threat to marine environments, existing legal structures under the UN Law of the Sea and the LC-LP provided an obvious route toward regulation and offered some degree of international consistency for the assessment of research and its impacts. In the case of atmospheric modification, an appropriate regulatory umbrella is harder to identify. Nevertheless, the fact that, under the LC-LP, the regulation of ocean fertilisation developed from a simple statement of concern to a permanent legal measure applicable at a global scale within just six years shows what can be achieved through effective co-operation between countries, even when complexity and uncertainties are high. If a suitable equivalent institution can be identified, there is no fundamental reason why an effective governance regime for research could not also be developed for atmospheric concepts.

Greenpeace has long maintained the view that any moves to deploy geoengineering as a strategy to try to counteract climate change would neither be sensible nor sustainable. In its most recent assessment of the possible impacts of geoengineering on natural systems, the Convention on Biological Diversity concluded that “changes in ocean productivity through large-scale fertilisation would necessarily involve major changes to marine ecosystems, with associated risks to biodiversity” (11). Moreover, as IOC-UNESCO has stressed, “we have insufficient knowledge, let alone technique...to reverse any large scale, long term changes to ecosystems” (5).

From the outset, talk of geoengineering as a possible emergency escape route—or, even more worrying, a cheaper and simpler option to tackle climate change impacts—has also proven to be a distraction from the urgent work of cutting emissions of greenhouse gases as quickly and deeply as possible. Even in a post-Paris Agreement world, with a tightened ambition on temperature targets (12), geoengineering must not be seen as an alternative to cutting emissions or to preparing for adaptation to change already upon us.

Nevertheless, it seems inevitable that calls for more geoengineering research will become increasingly loud. We can decide to leave the design and conduct of that research to the scientists and talk of governance only as and when things move towards deployment, as, for example, implied under the so-called Oxford Principles, (13). Alternatively, we can take a more proactive approach to the development of effective governance for

all forms of geoengineering research, taking a lead from the example of the LC-LP in relation to ocean fertilisation. Given the nature and scale of the interventions proposed, the backdrop of uncertainty and unknowns and the propensity for unintended consequences, the latter seems to be by far the more defensible option.

References

1. N. Vaughan, T. Lenton, *Climatic Change* **109**, 745 (2011).
2. Secretariat of the Convention on Biological Diversity, *Geoengineering in Relation to the Convention on Biological Diversity: Technical and Regulatory Matters*, Technical Series No. 66 (CBD, Montreal, 2012).
3. The Royal Society, *Geoengineering the climate: science, governance and uncertainty*. RS Policy document 10/09 (Royal Society, London, 2009).
4. E. A. Parson, D. W. Keith, *Science* **339**, 1278 (2013).
5. D. W. R. Wallace *et al.*, *Ocean Fertilization. A Scientific Summary for Policy Makers* (IOC/UNESCO, Paris, 2010).
6. S. W. Chisholm, P. G. Falkowski, J. J. Cullen, *Science* **294**, 309 (2001).
7. Resolution LC-LP.1, adopted on 31 October 2008, see [www.imo.org/blast/blastDataHelper.asp?data_id=24337&filename=LC-LP1\(30\).pdf](http://www.imo.org/blast/blastDataHelper.asp?data_id=24337&filename=LC-LP1(30).pdf).
8. Resolution LC-LP.2, adopted on 14 October 2010, see www.imo.org/en/OurWork/Environment/LCLP/EmergingIssues/geoengineering/Documents/OFAssessmentResolution.pdf.
9. IMO (2013), *Marine geoengineering including ocean fertilization to be regulated under amendments to international treaty*, see www.imo.org/en/MediaCentre/PressBriefings/Pages/45-marine-geoengineering.aspx#.V2k4n4-cFjU.
10. S. Tilmes *et al.*, *Journal of Geophysical Research: Atmospheres* **118**, 11036 (2013).
11. Convention on Biological Diversity, *Update on climate geoengineering in relation to the convention on biological diversity: potential impacts and regulatory framework* (UNEP/CBD/SBSTTA/19/INF/2, 2015).
12. UNFCCC, *Paris Agreement* (2015). See http://unfccc.int/paris_agreement/items/9485.php
13. Oxford Geoengineering Programme, *The Oxford Principles* (2009). See www.geoengineering.ox.ac.uk/oxford-principles/principles.

Any moves to deploy geoengineering as a strategy to try to counteract climate change would neither be sensible nor sustainable.

DGL Article

Smoke and mirrors are not the solution to global warming

Alan Robock (Rutgers University, robock@envsci.rutgers.edu)

Geoengineering is the “deliberate large-scale manipulation of the planetary environment to counteract anthropogenic climate change” (1). Proposed schemes include carbon dioxide reduction (CDR) and radiation management (RM). CDR technology exists but is very expensive, and no facilities exist for doing it on a large scale. It presents very different engineering, scientific, governance, and ethical issues than RM. Here I focus on the most studied proposed RM scheme, artificial creation of stratospheric aerosol clouds. I use the term “geoengineering” to refer to that scheme (2).

Geoengineering is currently impossible. The technology does not exist, and there are serious questions as to whether it would be possible to create a cloud in the stratosphere that would have the desired effects. We can investigate the impacts of a geoengineering intervention by using analogues, in particular volcanic eruptions, to explore some of the resulting benefits and risks. We can also use climate models, that is, computer simulations that calculate the climate response to geoengineering scenarios. These are the same models that we use for weather forecasting and global warming climate simulations. They are validated with simulations of past climate, in particular the response to volcanic eruptions.

If there were a way to continuously inject SO_2 into the lower stratosphere, it would create a permanent cloud there, producing global cooling, stopping melting of the ice caps, and increasing the uptake of CO_2 by plants. A comparison of different proposed injection schemes, using airplanes, balloons, and artillery (Figure 1), shows that putting sulphur gases into the stratosphere would be comparatively inexpensive. But there are at least 27 reasons why stratospheric geoengineering may be a bad idea (Table 1). These include disruption of the Asian and



Figure 1. Proposed methods of stratospheric aerosol injection. A mountain top location would require less energy for lofting to stratosphere. Drawing by Brian West. Reprinted with permission from (5).

African summer monsoons, reducing precipitation to the food supply for billions of people; ozone depletion; no more blue skies; reduction of solar power; and rapid global warming if geoengineering stops. Furthermore, there are concerns about commercial or military control, and serious degradation of terrestrial astronomy and satellite remote sensing.

Clearly, the solution to the global warming problem is mitigation (reduction of emissions of gases and particles that cause global warming, primarily CO_2). Society will also need to adapt to impacts that are already occurring. Whether geoengineering should ever be used will require an analysis of its benefits and risks, as compared to the risks of not implementing it. Research so far has

pointed out both benefits and risks from geoengineering and has shown that it is not a solution to the global warming problem, but at some time in the future, despite mitigation and adaptation measures, society may be tempted to try to control the climate to avoid dangerous impacts. Much more research on geoengineering is needed for society to be able to make informed decisions about the fate of Earth, the only planet in the universe known to sustain life.

The audacious idea of controlling Earth's climate brings up ethical and governance issues. The fundamental question is that of where to set the planet's thermostat. Who would decide how to carry out geoengineering? What values would be used to decide? For whose benefit would this decision be made: for those controlling the geoengineering; for the entire planet, however defined; for the benefit of those most at risk; only for humans; or taking into account the rest of the natural biosphere? These decisions are in the realms of politics and power and are different from testable scientific hypotheses. But scientific evaluations of the benefits, risks, and uncertainties of various proposals should, in an ideal world, inform decisions about implementation of geoengineering.

Ethical and governance decisions about geoengineering need to differentiate between research and deployment. As for geoengineering research, there have been many recent recommendations that it be enhanced, most recently from the U.S. National Academy of Sciences (3). But is such research ethical? Does it take resources away from other more useful pursuits? Is it yet another way for developed countries to continue to run the world to benefit themselves? Does the knowledge that this research is ongoing reduce whatever political drive there is toward mitigation because geoengineering will be seen as an easier solution to global warming? Does geoengineering research in a laboratory or a computer, with no emissions to the environment, have different ethical issues from outdoor research in which sulphur is emitted into the stratosphere? Would the existence of the technology enable hasty, politically-driven decisions to deploy? Is geoengineering research merely a smokescreen for weapons development? Or would it be unethical not to investigate a technology that may prevent widespread dangerous impacts of rising greenhouse gas concentrations? Would it be unethical not to provide policymakers with detailed information about the benefits and risks of various geoengineering proposals so that they can make informed decisions about implementation? Would it be unethical not to

develop the technology to carry out geoengineering, both so that the costs and efficacy can be determined (maybe it will prove impossible or much too expensive or dangerous), and to have the designs available so that it could be rapidly implemented if needed?

Certainly if the research itself were dangerous, directly harming the environment, this would bring up ethical concerns. To test whether there were a climate response or whether existing sulphuric acid cloud droplets would grow in response to additional emissions would require very large emissions, essentially amounting to implementation of geoengineering, and would therefore be unethical. But what about flights to spray a little SO₂ or other sulphur species and then observe how particles would grow or the response of ozone? Although no such governance now exists, any such outdoor experiments need to be evaluated by an organisation, like a United Nations commission, independent from the researchers, that evaluates an environmental impact statement from the researchers and determines that the environmental impact would be negligible, as is done now for emissions from the surface. Additional monitoring capabilities would be needed. There would also need to be enforcement of the limits of the original experiment, so that it would not be possible to expand the experiment in light of inconclusive results.

To make decisions about ethics requires a declaration of values, unlike in the physical sciences, where nature follows accepted laws such as conservation of energy. The above conclusions are based on the following principles: curiosity-driven indoor research cannot and should not be regulated, if it is not dangerous; emissions to the atmosphere, even for scientific purposes, should be prohibited if they are dangerous; and any results from geoengineering research need to be governed in the same way as all other dangerous human inventions, such as ozone depleting substances and nuclear weapons.

I have previously concluded that "in light of continuing global warming and dangerous impacts on humanity, indoor geoengineering research is ethical and is needed to provide information to policymakers and society so that we can make informed decisions in the future to deal with climate change... Outdoor geoengineering research, however, is not ethical unless subject to governance that protects society from potential environmental dangers" (4). Eventual decisions about deployment will need to consider the relative benefits and risks, which will be determined by research. All

If the research itself were dangerous, directly harming the environment, this would bring up ethical concerns.

these potential benefits and risks (**Table 1**) will need to be quantified. Because some can never be quantified, I am sceptical that geoengineering will ever be deployed. Of course, real-world decisions are made without full knowledge and sometimes under pressure from extraordinary events. Much more research in stratospheric geoengineering, conducted transparently and published openly, is needed for future policy decisions to be as informed as possible.

Even at this late date, a global push to rapid decarbonisation by imposing a carbon tax will stimulate renewable energy and allow solar, wind, and newly developed energy sources to allow civilisation to prosper without using the atmosphere as a sewer for CO₂. Adaptation will reduce some negative impacts of global warming. Geoengineering does not appear to be a panacea; geoengineering research should be in addition to strong efforts toward mitigation, and should not be a substitute. In fact, geoengineering may soon prove to be so unattractive that research results will strengthen the push toward mitigation.

Table 1. Benefits and risks of stratospheric geoengineering. The effects that are observed after volcanic eruptions are indicated by an asterisk (*). Updated from (2).

Benefits	Risks
1. Reduce surface air temperatures*, which could reduce or reverse negative impacts of global warming, including floods, droughts, stronger storms, sea ice melting*, land-based ice sheet melting, and sea level rise*	1. Drought in Africa and Asia*
2. Increase plant productivity*	2. Perturb ecology with more diffuse radiation*
3. Increase terrestrial CO ₂ sink*	3. Ozone depletion, with more UV at surface*
4. Beautiful red and yellow sunsets*	4. Whiter skies*
5. Unexpected benefits	5. Less solar energy generation*
	6. Degrade passive solar heating
	7. Environmental impact of implementation
	8. Rapid warming if stopped*
	9. Would not stop ice sheets from melting
	10. Cannot stop effects quickly
	11. Human error
	12. Unexpected consequences
	13. Commercial control
	14. Military control of technology
	15. Conflicts with current treaties
	16. Whose hand is on the thermostat?
	17. Degrade terrestrial optical astronomy*
	18. Affect stargazing*
	19. Affect satellite remote sensing*
	20. Societal disruption, conflict between countries
	21. Effects on airplanes flying in stratosphere*
	22. Effects on electrical properties of atmosphere
	23. More sunburn (from diffuse radiation)
	24. Continued ocean acidification
	25. Impacts on tropospheric chemistry
	26. Moral hazard – the prospect of it working would reduce drive for mitigation
	27. Moral authority – do we have the right to do this?

Acknowledgments

I thank Brian West for drawing Figure 1. Supported by U.S. National Science Foundation grants AGS-1157525 and GEO-1240507.

References

1. J. G. S. Shepherd et al., *Geoengineering the climate: Science, governance and uncertainty*, RS Policy Document 10/09 (Royal Society, London, 2009).
2. Parts of this article are condensed from A. Robock, Stratospheric aerosol geoengineering, *Issues Env. Sci. Tech.* **38**, 162-185 (2014).
3. M. K. McNutt (Chair), Committee on Geoengineering Climate: Technical Evaluation and Discussion of Impacts, *Climate Intervention: Reflecting Sunlight to Cool Earth*, (U.S. National Academy of Sciences, Washington, DC, 2015).
4. A. Robock, *Peace and Security* **4**, 226 (2012).
5. A. Robock, A. B. Marquardt, B. Kravitz, G. Stenchikov, *Geophys. Res. Lett.* **36**, L19703 (2009).

Forthcoming meeting

Environmental chemistry of water, sediment and soil: early-career researcher meeting

When: Monday 14th November 2016

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

Join us for this one-day meeting aimed at PhD students, postdoctoral researchers, and early-career scientists in industry. You will have the opportunity to share your research in a supportive environment, network with fellow early career scientists, and hear about the career opportunities available to environmental chemists.

Prizes will be awarded for the best oral and poster presentations.

Contact: Tom Sizmur, University of Reading (t.sizmur@reading.ac.uk)

Forthcoming meeting

What's new in the analysis of complex environmental matrices?

When: Friday, 3 March 2017

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

This event is the third in the series of highly successful biennial meetings jointly organised by the RSC's Environmental Chemistry Group and Separation Science Group (Analytical Division). The meeting will describe recent developments in the analysis of various complex matrices, highlighting different analytical (GC, LC, MS, NMR) approaches.

For reports from previous meetings see:

ECG *Bulletin*, July 2015

http://www.rsc.org/images/ECG-Bulletin-July-2015-final_tcm18-246976.pdf

ECG *Bulletin*, July 2013

http://www.rsc.org/images/ECG-Bulletin-July-2013_tcm18-233368.pdf

Contact: Roger Reeve, University of Sunderland, roger.reeve@sunderland.ac.uk
Graham Mills, University of Portsmouth, graham.mills@port.ac.uk

Waste classification

James Lymer (Wardell Armstrong, jlymer@wardell-armstrong.com)

The UK, along with other industrialised nations, has a legacy of large scale waste generation from domestic, commercial and industrial sectors. Over the past century, most of this waste has been disposed of in landfill. Waste requires appropriate storage and robust disposal, recycling and recovery options, because poor practices can result in air, soil and groundwater pollution, with potential risks to human health and the environment. This Environmental Brief outlines the broad requirements of waste classification in the UK.

The classification of whether a waste is hazardous or non-hazardous involves the skills and knowledge of chemists who understand the behaviour and toxicity of chemicals. They must evaluate the results of chemical testing, based on an understanding of the analytical methods used and the information they provide, to assess potential hazardous properties.

Careful and robust classification of waste materials is important given the strict controls required for storage, treatment and disposal of hazardous waste, in addition to the higher costs involved compared with other waste types. It is also important to ensure that wastes are disposed of in the correct landfill sites. Non-hazardous waste should not be disposed of in hazardous waste landfill sites because limited disposal volume is available in the UK. On the other hand, disposal of hazardous waste in landfills not designed to accept it can result in potential risks to the environment.

Legislation and regulations

The EU Waste Framework Directive (WFD), implemented in the UK via domestic legislation, sets out what waste is and how it should be managed. Within the directive, the List of Wastes (LoW) provides more detail on the types of wastes. The assessment and classification of waste is derived from Annex III of the Waste

Framework Directive and applies to wastes within the scope of this directive and domestic UK legislation (1).

During 2015, there were several significant legislative changes that affect the classification of waste, including: amendments to the List of Wastes; criteria for persistent organic pollutants; major revision of hazardous properties in the WFD; and the adoption of the Classification, Labelling and Packaging Regulation (CLP) for chemicals. Chemists will likely be familiar with the CLP Regulation which applies the United Nations' Globally Harmonised System on the classification and labelling of chemicals across all EU countries. This is a key resource in identifying substances with hazardous properties in waste materials. To take account of these changes, the Environment Agency and other agencies have revised technical guidance in the UK, which is presented in *WM3, Guidance on the classification and assessment of waste* (1st edition 2015) (2, 3).

Waste types

The List of Wastes is divided into twenty chapters based on separate sectors that produce the waste. Each individual waste entry is provided with a six-digit waste code. The initial classification of a waste involves identifying how it is classified in the List of Wastes and assigning a code. Wastes that fall into mirror entry codes require further assessment as discussed below.

There are three key types:

1. "absolute" hazardous entries — wastes that are always hazardous. For example, **07 01 03*** refers to organic halogenated solvents, washing liquids and mother liquors;
2. "absolute" non-hazardous entries — wastes that are always non-hazardous. For example, **05 01 16** refers to sulphur-containing wastes from petroleum desulphurisation; and
3. "mirror" entries — wastes that may be hazardous or non-hazardous depending on further assessment. Examples include **19 01 11*** (bottom ash and slag containing hazardous substances) and **19 01 12** (bottom ash and slag other than those mentioned in **19 01 11**).

A hazardous waste is defined as a waste that has one or more of the fifteen specified hazardous properties listed

in Annex III of the WFD or contains persistent organic pollutants above specified concentration limits.

Mirror entry

To determine whether a mirror entry waste is hazardous or not, its chemical composition needs to be known. There are three main ways to determine the composition of the waste: manufacturer's information; using knowledge of the process chemistry involved to elucidate the composition; or sampling and testing of the waste to determine its composition. For wastes of unknown chemical composition, such as soils and stones from contaminated sites (see below), sampling and testing of the waste and subsequent data interpretation is the primary means of determining the waste classification.

For soil from potentially contaminated sites, the chemical composition of the soil is often available from intrusive site investigation work carried out as part of redevelopment works. The redevelopment works may generate soils requiring off-site disposal or re-use and waste classification of this material could be as either **17 05 03*** (soil and stones containing hazardous substances) or **17 05 04** (soil and stones other than those mentioned in **17 05 03**).

Example

Fly ash is a waste generated from the combustion of coal at power stations and other combustion plants. From the List of Wastes, the entry can be considered to be **10 01 16*** (fly ash from co-incineration containing hazardous substances) or **10 01 17** (fly ash from co-incineration other than those mentioned in **10 01 16**).

Heavy metals such as zinc are a typical component of combustion ash. Given the combustion process, zinc oxide is a potential form of zinc in the waste. Zinc oxide is a hazardous substance possessing Hazard Statement Codes which are appropriate to Ecotoxicity (Hazardous Property 14 or HP14).

Periodic sampling and testing of batches of ash would yield the total zinc concentration, but this represents the cation and does not identify the exact hazardous substance. For example, a total zinc concentration of 3,000 ppm in the waste would represent ca. 3,750 ppm of equivalent zinc oxide. These concentrations are above the thresholds for HP14; through further assessment using the appropriate ecotoxicity equations, an assessor would classify the waste as hazardous (4).

Landfill waste acceptance criteria

Once waste has been classified as hazardous or non-hazardous, it may be destined for disposal at a landfill

site. The Landfill Directive requires that waste is properly characterised and meets specific Waste Acceptance Criteria (WAC) prior to disposal at a landfill site. WAC includes a combination of concentration limits for total composition and leachable content to ensure that waste is properly characterised. Landfills are classified according to whether they can accept hazardous, non-hazardous or inert wastes (5). The EU has not, so far, set limit values for non-hazardous wastes received at a non-hazardous landfill site (6).

A common cause of confusion is the use of Waste Acceptance Criteria to classify the waste as hazardous or non-hazardous. WAC analysis is only used for disposal of material to landfill and does not allow classification or meaningful assessment as to whether a waste may be hazardous or non-hazardous.

This brief outlines a general approach to waste classification. It is for information purposes only, is not to be relied upon and is the opinion of the author. Waste classification must be carried out by an appropriately competent and qualified person and in accordance with UK legislation and Regulatory and Technical Guidance.

References and notes

1. See www.gov.uk/waste-legislation-and-regulations
2. See www.gov.uk/how-to-classify-different-types-of-waste
3. See www.gov.uk/government/publications/waste-classification-technical-guidance
4. A single substance is unlikely to be representative of a waste, particularly combustion ash, which may contain numerous hazardous substances including heavy metals and polycyclic aromatic hydrocarbons. Their inclusion would result in a more complex waste assessment.
5. Inert waste "means waste that does not undergo any significant physical, chemical or biological transformations ... Inert waste will not dissolve, burn or otherwise physically or chemically react, biodegrade or adversely affect other matter with which it comes into contact in a way likely to give rise to environmental pollution or harm human health. The total leachability and pollutant content of the waste and the ecotoxicity of the leachate must be insignificant, and in particular not endanger the quality of surface water and/or groundwater." Definition from www.gov.uk/government/publications/waste-acceptance-at-landfills, page 16.
6. See www.gov.uk/government/publications/waste-sampling-and-testing-for-disposal-to-landfill

The relative-rate technique for determining rate constants

Martin King (Royal Holloway, University of London, m.king@rhul.ac.uk)

Many chemical reactions in environmental media are kinetically controlled, that is, their concentration in the environment is limited by their rate of reaction. This is especially true in the field of atmospheric chemistry. Measurement of the rate constant for a reaction is thus important. One method made popular by Atkinson (1) in the atmospheric sciences is the relative-rate technique, which is particularly useful in cases where the concentrations of one reactant are difficult to measure.

The relative-rate technique measures the loss of a substrate compound (S) relative to that of a reference compound (R), both mixed in the same reaction vessel in the presence of a reactive species. With knowledge of the rate constant, k , for reaction between the reactive species and R, one can infer the rate constant of the reactive species with S. The advantage is that reactive species, which often have short lifetimes and are present in very low concentrations, need not be measured. The vessel may be an atmospheric air parcel, an ice core or a reaction chamber. In the following, I consider the reactions of an important night-time atmospheric oxidant, the nitrate radical NO_3 :



Derivation

The rate equations can be written as

$$\frac{d\ln[S]}{dt} = -k_A[\text{NO}_3] \quad (1)$$

$$\frac{d\ln[R]}{dt} = -k_B[\text{NO}_3] \quad (2)$$

Equations (1) and (2) are integrated to

$$\ln[S]_t = -k_A \int_{t=0}^t [\text{NO}_3] dt + \ln[S]_{t=0} \quad (3)$$

$$\ln[R]_t = -k_B \int_{t=0}^t [\text{NO}_3] dt + \ln[R]_{t=0} \quad (4)$$

and rearranged to

$$\ln\left(\frac{[S]_{t=0}}{[S]_t}\right) = -k_A \int_{t=0}^t [\text{NO}_3] dt \quad (5)$$

$$\ln\left(\frac{[R]_{t=0}}{[R]_t}\right) = -k_B \int_{t=0}^t [\text{NO}_3] dt \quad (6)$$

Equations (5) and (6) can be equated to give

$$\ln\left(\frac{[S]_{t=0}}{[S]_t}\right) = \frac{k_A}{k_B} \ln\left(\frac{[R]_{t=0}}{[R]_t}\right) \quad (7)$$

Thus, a plot of $\ln([S]_{t=0}/[S]_t)$ versus $\ln([R]_{t=0}/[R]_t)$ should be a straight line with a gradient of k_A/k_B and an intercept of zero. Knowledge of k_B allows k_A to be determined. An example of such a plot is shown in **Figure 1**, where the reaction rate constant for reaction of the NO_3 radical with some unsaturated carbonyls is calculated relative to the reaction with ethane (2).

Adaptation to the tracer

When sampling a reaction chamber for the concentrations of S and R, imperfect mixing in the changer or loss of R and S owing to the measurement technique may affect the determination of k_A/k_B . Imperfect mixing or loss of material on analysis can be compensated by an internal standard chemical compound I. The concentration of this internal standard [I] is used to account for any dilution of concentration of S and R by sampling.

The term $D_t = \ln\left(\frac{[I]_{t=0}}{[I]_t}\right)$ can be used to adapt equation (7) to

$$\ln\left(\frac{[S]_{t=0}}{[S]_t}\right) - D_t = \frac{k_A}{k_B} \left(\ln\left(\frac{[R]_{t=0}}{[R]_t}\right) - D_t \right) \quad (8)$$

Thus, a plot of $\ln([S]_{t=0}/[S]_t) - D_t$ versus $\ln([R]_{t=0}/[R]_t) - D_t$ will be a straight line with a gradient of k_A/k_B and an intercept of zero. An example is shown in (3).

Regression and analysis of errors

The regression used in Figure 1 to calculate the gradient and intercept must consider the errors in the ordinate and the abscissa. More information can be found in (4). The error in the quantity $\ln([S]_{t=0}/[S]_t) - \ln([I]_{t=0}/[I]_t)$ can be calculated by propagation of errors (5) as

$$\delta_Y = \sqrt{\left(\frac{\delta_S}{[S]_{t=0}}\right)^2 \left(1 + \left(\frac{[S]_{t=0}}{[S]_t}\right)^2\right) + \left(\frac{\delta_I}{[I]_{t=0}}\right)^2 \left(1 + \left(\frac{[I]_{t=0}}{[I]_t}\right)^2\right)} \quad (9)$$

First-order loss of substrate

In some reaction systems the substrate S may not be stable, may irreversibly react with a wall, or may decay away, i.e. it has a first-order loss



Following the same analysis as in the derivation section yields

$$\frac{1}{(t-t_0)} \left(\ln \left(\frac{[S]_{t=0}}{[S]_t} \right) - D_t \right) = \frac{k_A}{k_B(t-t_0)} \left(\ln \left(\frac{[R]_{t=0}}{[R]_t} \right) - D_t \right) + k_c \quad (10)$$

The equation now requires the time, t since the reaction began at time t_0 to be recorded. Plotting the left-hand side term in equation (10) against the first term on the right yields a straight line with an intercept of k_c . Plotting data in the form of equation (10) is a method of testing if S is stable in the reaction system.

Concentration of reactive intermediate

There is an issue with the above method of analysis of k_A when there is an extra first-order loss which can be seen during the derivation of (10),

$$\frac{1}{k_A} \left(\ln \left(\frac{[S]_{t=0}}{[S]_t} \right) - D_t \right) - k_c(t-t_0) = \int_{t=0}^t [NO_3] dt \quad (11)$$

If the nitrate radical concentration, $[NO_3]$, does not change during the experiment, then points on a plot

$$\frac{1}{(t-t_0)} \left(\ln \left(\frac{[S]_{t=0}}{[S]_t} \right) - D_t \right) \text{ versus } \frac{1}{(t-t_0)} \left(\ln \left(\frac{[R]_{t=0}}{[R]_t} \right) - D_t \right)$$

will cluster together and make the determination of k_A/k_B difficult. More information can be found in (6).

Conclusion

The relative-rate method is a powerful method for determining rate constants needed for lifetime calculations and environmental persistence, especially when one of the reactants—in the above example, $[NO_3]$ —is very difficult to measure. The method is less precise than an absolute kinetic determination, because the

uncertainty of the reference reaction influences the uncertainty of the measured reaction.

References

1. R. Atkinson, *Chem. Rev.*, 1986, 86, 69.
2. C. E. Canosa-Mas, S. Carr, M. D. King, D. E. Shallcross, K. C. Thompson, R. P. Wayne, *Phys. Chem. Chem. Phys.* **1**, 4195 (1999).
3. C. E. Canosa-Mas, M. D. King, P. J. Scarr, K. C. Thompson, R. P. Wayne *Phys. Chem. Chem. Phys.* **1**, 2929 (1999).
4. T. Brauers, B. J. Finlayson-Pitts, *Int. J. Chem. Kinet.* **29**, 665 (1997).
5. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
6. C. E. Canosa-Mas, M. D. King, D. E. Shallcross, R. P. Wayne, *Phys. Chem. Chem. Phys.* **1**, 2411 (1999).
7. M. King, DPhil Thesis, University of Oxford (1998).

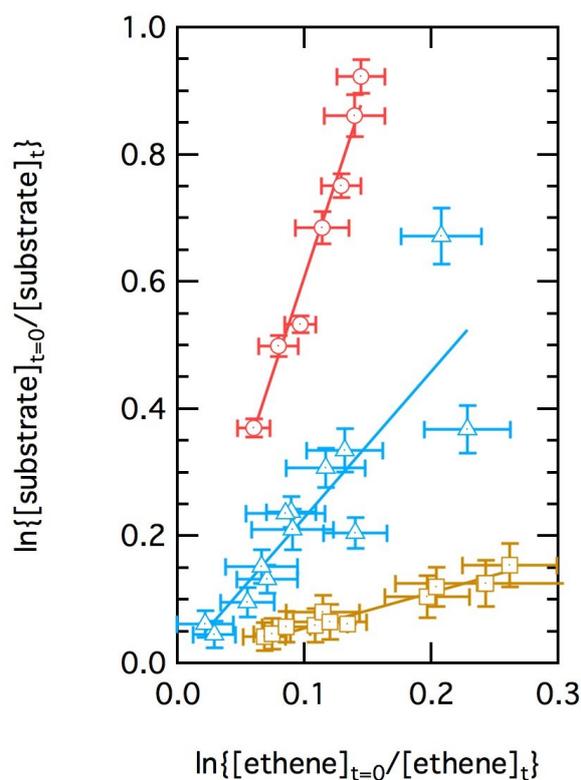


Figure 1. The relative-rate plot for the reaction of some alpha-beta carbonyls with nitrate radical, with ethane as a reference compound. Red circles, acrolein; blue triangles, methyl vinyl ketone; yellow squares, methyl acrylate. From (7).



Issues in Environmental Science and Technology

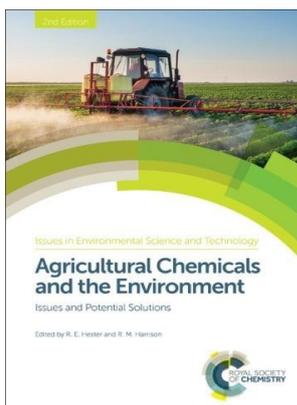
Series Editors: R. M. Harrison, University of Birmingham, UK | R. E. Hester, University of York, UK **ISSN:** 1350-7583

Overview

This series has been devised to tackle important environmental topics in response to the rapid growth of interest in this area and the need for authoritative reviews of such topics. Written by world experts in their specialised fields, the series presents a multidisciplinary approach to pollution and environmental science and, in addition to covering the chemistry of environmental processes, focuses on broader issues: notably economic, legal and political considerations.

Forthcoming titles from the Royal Society of Chemistry

Agricultural Chemicals and the Environment: Issues and Potential Solutions



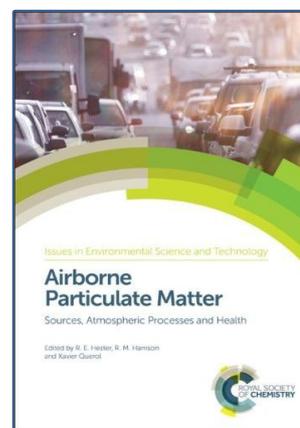
Agricultural production is in a period of rapid transformation which has seen an increase in the use of biotechnology, synthetic chemistry, biological chemicals and biopesticides. These disciplines are integrated with improvements in application technology, digital farming and the use of big data. Whilst offering unique opportunities to reduce potential environmental impacts, these advances also raise new environmental concerns. This book provides an overview of the changes occurring in the agricultural industry, highlighting opportunities to address impacts and indicating potential barriers to adoption of the technology. This new edition has been updated to include the very latest in agricultural developments, including organic farming and genetically modified crops. It is of interest to students and academics, as well as farmers and landowners and those working in legislation.

Hardback | 283 pages | 9781782626909 | 2016 | £67.50 | \$108.00

Airborne Particulate Matter: Sources, Atmospheric Processes and Health

The estimated health impacts and associated economic costs resulting from airborne particulate matter are substantial. Exposure to airborne fine particles ranks highly amongst preventable causes of disease. This book reviews the sources and atmospheric processes affecting airborne particulate matter and consequent impacts upon human health. Examining the latest information on the sources of particles in the atmosphere, both through direct emissions and atmospheric formation, the book also explores the methods which are used to estimate the contributions of different sources to airborne concentrations. Featuring case studies from recent assessments in Europe, the USA, China and India, the book provides a global overview of source apportionment. This comprehensive book is an important reference for policymakers and consultants working with pollution and human health, as well as academics working in atmospheric chemistry.

Hardback | 400 pages | 9781782624912 | 2016 | £67.50 | \$108.00





Energy and Environment Series

Editor in Chief: L. Peter, University of Bath, UK

Series Editors: H. Frei, Lawrence Berkeley National Laboratory, USA | R. Rinaldi, Imperial College London, UK |

T. Zhao, The Hong Kong University of Science and Technology, Hong Kong

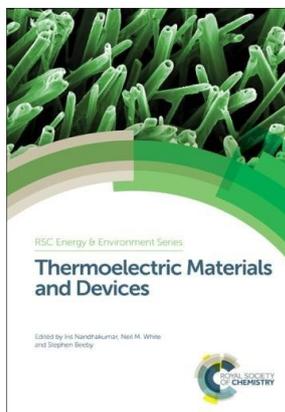
ISSN: 2044-0774

Overview

Energy lies at the heart of modern society, and it is critical that we make informed choices of the methods by which we convert and manage energy. This series provides up-to-date and critical perspectives on the various options that are available. The wide range of topics covered reflects the wealth of chemical ideas and concepts that have the potential to make an important impact in the search for sustainable energy. Books in this series form important references for chemical and material scientists, chemical and process engineers, energy researchers, bio-scientists and environmental scientists from across academia, industry and Government.

Forthcoming titles from the Royal Society of Chemistry

Thermoelectric Materials and Devices



Thermal energy harvesting is predicted to become a global, billion-pound market by 2020. This book provides a current perspective of recent developments and trends within thermoelectric materials and devices for power energy harvesting applications. The book highlights the potential of thermoelectrics in the context of a low carbon energy economy, and features in-depth coverage of a range of different fabrication methods for thermoelectric materials, including electrodeposition. Topics covered include layered and pseudo-layered materials, thermoelectric oxides, nano- and micro-fabrication techniques, high-throughput thermoelectric measurement techniques and power mining. This book is ideal for researchers and industrialists in materials science.

I. Nandhakumar, N. M. White and S. Beeby, University of Southampton, UK Hardback | 321 pages | 9781782623236 | 2016 | £159.00 | \$260.00

Browse our full range of books online at www.rsc.org/books.

If you are a member of the Royal Society of Chemistry you can save 35% on the list price.

Simply log in with your member log-in details and the discount will be applied automatically at the Bookshop checkout.