January 2012

Royal Society of Chemistry ISSN 1758-6224 (Print) 2040-1469 (Online)

Environmental Chemistry Group www.rsc.org/ecg

Bulletin

Tyndall Glacier, Rocky National Park, Colorado

In this issue

"*As a dam built across a river causes a local deepening of the stream, so our atmosphere, thrown as a barrier across the terrestrial rays, produces a local heightening of the temperature at the Earth's surface.*" John Tyndall, *Contributions to Molecular Physics in the Domain of Radiant Heat*, Longmans, Green, & Co., London, 1872, p 117. Tyndall's interest in the structure of glaciers had two consequences: he became an accomplished mountaineer; and he appreciated the implications for the climate of his 1859 experiments on the absorption of thermal radiation by water vapour and by CO_2. The life and work of **John Tyndall** and several other pioneering investigators of the science of the environment – including **Arie Jan Haagen-Smit**, **Robert Angus Smith** and **Frederick Challenger** – were celebrated at a symposium organised by the RSC's ECG and Historical Group in October 2011. Details of the proceedings of this meeting are reported on pp 5-28 of this issue.

Also

News of the distribution of future editions of the **ECG *Bulletin***. A report of a recent meeting on the **toxicology of metallic nanoparticles** organised by the RSC's Toxicology Group. And details of the **2012 ECG Distinguished Guest Lecture** and accompanying symposium at Burlington House, London in March.

RSC | Advancing the Chemical Sciences

Contents

ECG *Bulletin*

Published biannually by the Royal Society of Chemistry's (RSC) Environmental Chemistry Group (ECG), Burlington House, Piccadilly, London, W1J 0BA, UK

Editors

Rupert Purchase
38 Sergison Close, Haywards Heath, West Sussex RH16 1HU
rp@rupertpurchase,demon.co.uk

Roger Reeve
University of Sunderland
roger.reeve@sunderland.ac.uk

Editorial Board

Environmental Chemistry Group

www.rsc.org/ecg

The RSC's Environmental Chemistry Group (ECG) considers all aspects of the complex relationships between chemistry and the environment. The ECG aims to understand the behaviour of chemical species in the water, soil and atmospheric environments; exploring their sources, reactions, transport and in particular their effects on each of these environments.

Chair

Leo Salter,

Rainscapper@hotmail.com

Vice-Chair

Bill Bloss, University of Birmingham

w.j.bloss@bham.ac.uk

Honorary Secretary

James Lymer, Wardell Armstrong LLP, Sheffield

jlymer@wardell-armstrong.com

Honorary Treasurer

Jo Barnes, University of the West of England, Bristol

annaoj_senrab@hotmail.com

Registered Charity Number 207890

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

Chairman's report for 2011

ECG Symposia: 'The Nitrogen Cycle' was the topic for the **2011 ECG DGL & Symposium**, held at Burlington House on March 9th. This well-attended event, supported in part by the RSC Environment, Sustainability and Energy Division, focussed on the effects of nitrogen speciation and utilisation on man and the natural environment. A report of the meeting may be found in the September 2011 edition of the ECG *Bulletin*, and the speakers' PowerPoint presentations are on the ECG web pages.

The **2012 DGL & Symposium ('Energy, Waste and Resources – three sides of the same coin?')** will take place from 12.00 on Wednesday, March 14th in Burlington House. The 2012 Distinguished Guest Lecturer is Professor Paul Williams (University of Leeds).

On October 26th 2011 at Burlington House, the ECG and the RSC Historical Group held a combined meeting, **'Environmental chemistry: a historical perspective'**. Good speakers and an appreciative and engaged audience helped to make this a fascinating event. Full details of the proceedings of the meeting are in this issue of the ECG *Bulletin*.

ECG Atmospheric & Environmental Chemistry Forum: The ECG has previously organised two Atmospheric & Environmental Chemistry forums in 2009 and in 2010, respectively, for PhD students and early career post-doctoral researchers. Feedback from the last forum in 2010 was unequivocally supportive of holding the event, but suggested that future forums should be scheduled every 18 months. Hence no forum was held in 2011, but the ECG is organising another Atmospheric & Environmental Chemistry Forum for the spring of this year, 2012.

News of the Royal Society of Chemistry: In November 2011, the RSC General Assembly was held in Birmingham and Leo Salter chaired a meeting of Interest Group representatives. A discussion took place about awarding full membership of the RSC (i.e. MRSC) to individuals who might not have had a 'complete' training as chemists – as recognised professionally by the designation of Chartered Chemist (CChem). It was thought that offering MRSC would better represent the growth in the multi-disciplinary facets of chemistry in the 21st Century – one which has been recognised through the creation of the new Divisions predicated on multi-disciplinary interests. The benefits of the RSC being an inclusive organisation were perceived to be strong, and the current Associate Membership status was not seen as appropriate at this time. These views will be forwarded to the RSC Council. This year's General Assembly demonstrated that within the RSC:

- The range of international activities in publishing and education is wide, growing and vibrant.
- National activities are under constant review with new structures being developed and new plans being made for increasing support for the regions.
- There is increasing thought being given to engaging with policy makers and to providing decision makers with accurate information regarding the cultural, economic and strategic value of the chemical sciences.

ECG Committee: The Environmental Chemistry Group (ECG) would like to recruit additional members to join the committee in 2012 and 2013. ECG committee members fill the traditional Interest Group Officer posts (Chair, Vice-Chair, Secretary and Treasurer) for a defined period and in addition they take on responsibility for organising scientific meetings for the Group. ECG committee meetings are held three to four times a year at the Royal Society of Chemistry, Burlington House, London. If you are interested in contributing to the ECG committee, please contact James Lymer [jlymer@wardell-armstrong.com] or Bill Bloss [w.j.bloss@bham.ac.uk] for an informal discussion.

At the next ECG AGM (March 14th 2012), the following committee changes will be proposed: **Bill Bloss** (currently Vice-Chair) to become Chair until 2014. **Leo Salter** to move from Chair to Vice-Chair, and **James Lymer** (currently Secretary) to become Vice-Chair at the 2013 AGM and then Chair in 2014.

Future of the ECG *Bulletin*: The ECG *Bulletin* has been issued as a printed edition since its inauguration (as the *ECG Newsletter*) in January 1995. However, with the recent changes to RSC Interest Group funding, increased membership numbers, and rising distribution costs relative to ECG income, the ECG committee has reviewed the production and distribution costs and it is with regret that the **printed edition of the ECG *Bulletin*** will cease production following this edition (January 2012). The electronic version of the ECG *Bulletin*, the **ECG e-Bulletin**, will continue to be available from the ECG web pages. For all future and past editions of the ECG *Bulletin*, members are directed to the ECG website where the **ECG e-Bulletin** (as a pdf) is available for viewing or for download. The link to the ECG website will be emailed to members when the ECG *Bulletin* is issued around January and July each year. **All members** should ensure that the RSC have their current email address so they can be alerted when the ECG *Bulletin* is added to the ECG web pages. RSC member's details can be updated online on the RSC website or by contacting the membership department at membership@rsc.org

More gloom for Gaia. The state of greenhouse gases in the atmosphere based on global observations through 2010: The latest analysis of observations from the World Meteorological Organization Global Atmosphere Watch Programme shows that the globally averaged mixing ratios of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) reached new highs in 2010, with CO_2 at 389.0 ppm, CH_4 at 1808 ppb and N_2O at 323.2 ppb. These values are greater than those in pre-industrial times (before 1750) by 39%, 158% and 20%, respectively. Atmospheric increases of CO_2 and N_2O from 2009 to 2010 are consistent with recent years, but they are higher than both those observed from 2008 to 2009 and those averaged over the past 10 years. Atmospheric CH_4 continues to increase, consistent with the past three years. The US National Oceanic and Atmospheric Administration Annual Greenhouse Gas Index shows that from 1990 to 2010 radiative forcing by long-lived greenhouse gases increased by 29%, with CO_2 accounting for nearly 80% of this increase. Radiative forcing of N_2O exceeded that of CFC-12, making N_2O the third most important long-lived greenhouse gas. The major anthropogenic source of N_2O to the atmosphere is the use of nitrogen containing fertilizers (including manure), which have profoundly affected the global nitrogen cycle. (Source: *WMO Greenhouse Gas Bulletin***,** No. 7: 21st November 2011).

LEO SALTER
January 2012

Tellus (the Roman earth-goddess). Roman relief, 13-9 BC. Royal Cast Collection, Copenhagen

---

RSC Energy and Environment Series

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. The **RSC Energy and Environment Series** will provide an up-to-date and critical perspective on the various options that are available. Chemistry has a central role to play in the planning and development of sustainable energy scenarios, and the wide range of topics that will be covered in the series will reflect the wealth of chemical ideas and concepts that have the potential to make an important impact in mankind's search for a sustainable energy future.

Series Titles

Molecular Solar Fuels

Thomas J Wydrzynski (Editor), Warwick Hillier (Editor)
2011; £144.99

Chemical and Biochemical Catalysis for Next Generation Biofuels

Blake A Simmons (Editor)
2011; £125.99

Energy Crops

Nigel G Halford (Editor), Angela Karp (Editor)
2010; £139.99

Innovations in Fuel Cell Technologies

Robert Steinberger-Wilckens (Editor), Werner Lehnert (Editor)
2010; £121.99

Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals

Mark Crocker (Editor)
2010; £139.99

Environmental Chemistry: A Historical Perspective

A report of the meeting organised by the Royal Society of Chemistry's Environmental Chemistry Group and Historical Group at the Chemistry Centre, Burlington House on Wednesday, October 26th 2011.

Environmental change and its consequences for our future energy needs have dominated much of the political debate of the first two decades of this century. This one-day symposium was an opportunity to recognise some of the scientists whose work gives us an understanding of the chemistry of the environment and underpins the concern about the impact of anthropogenic activity. Around 65 delegates attended the meeting and throughout the event their participation and questions were admirable. There were six speakers, and **Professor Michael Pilling** (Emeritus Professor at the University of Leeds) opened and chaired the proceedings.

The opening speaker was **Professor Simon Tett** from the University of Edinburgh who spoke on "Anthropogenic CO_2 and climate change – a historical perspective" and whose aim was to "give a sense of the historical development of climate change studies over the last 150 years." During the latter part of the 19th century data from Tyndall's experiments in the 1860s led to a general consensus that water vapour, carbon dioxide and methane were such strong absorbers in the infra-red region that small changes in their concentrations would have little impact on the earth's temperature, but this was challenged when Arrhenius (1896) showed that increases or decreases in carbon dioxide in the atmosphere would be coupled with changes in atmospheric water vapour concentrations and would produce a change in temperature. For example, if atmospheric CO_2 concentrations halved then 5K cooling would occur. In the late 1930s a collation of observational data by Callendar indicated a small increase in Global Average Near-Surface Temperature and although these data were not generally accepted they did give an impetus to further work. Roger Revelle and Hans Suess made an estimate of fossil fuel carbon dioxide inputs into the atmosphere using ^{14}C measurements of 'old' and 'modern' wood and they suggested that this 'extra' anthropogenic carbon dioxide was taken up by the oceans. However, Roger Revelle later threw doubt on the idea of ocean take-up by showing that ocean buffering meant that the upper ocean would then emit the CO_2 back to the atmosphere. And Charles Keeling's global measurements of carbon dioxide (which culminated in the start of the Mauna Loa record) showed increases in carbon dioxide at the South Pole and this supported the idea that anthropogenic carbon dioxide ended up in the atmosphere and not the ocean. By 1965 reports were appearing in the US which suggested that anthropogenic gases may cause climate change, and ice-core data showed that changes in greenhouse gases such as carbon dioxide paralleled ice ages. At this stage basic General Circulation Models began to be developed which used the principles of conservation of momentum, mass and energy, and equations of state together with exchanges across interfaces (e.g. air-sea interface) to develop the understanding of the effects of anthropogenic carbon dioxide as an emergent phenomenon – a task which has become much better refined as the computational power available increased by a factor of 16 during every decade since the 1960s. Best 'current' estimates (2007 IPCC) for the effects of anthropogenic carbon dioxide are that carbon dioxide was responsible for half of the enhanced climate effect, that a rise of 0.3K per decade is predicted with an associated 3–to-10 cm per decade rise in sea level, and that there has been an 0.3-to-0.6 K increase in the global mean temperature over the last century.

Professor Frank James (The Royal Institution) gave a talk on the life of John Tyndall ("Held fast in the iron grip of frost': field and laboratory in John Tyndall's discovery of the Greenhouse Effect."). John Tyndall (1820-1893) was born into the protestant persuasion in Ulster but later became an agnostic. He did not go to university but joined the Ordnance Survey, and after surveying in Ireland and Lancashire he took advantage of the boom in railway building in the 1840s to become a railway surveyor. Subsequently he joined Queenwood College in Hampshire to teach mathematics; the College was unusual for the period in that it taught science and was philosophical based on utopian socialism. At that time, Edward Frankland, an early proponent of organo-metallic chemistry taught chemistry there and he became a close friend of Tyndall. They both decided to go to university – first to Marburg to work with Bunsen and then to Berlin where Tyndall studied diamagnetism and the magneto-optical effect recently discovered by Faraday. In 1851 after working with Magnus at the University of Berlin Tyndall's money ran out and he returned to Queenwood where Sabine and Jones from the Royal Institution befriended him so that in 1853 he was invited to give one of the Friday evening lectures at the RI. In a short time his lecturing became famous and he was appointed as Professor of Natural Philosophy at the RI and, although being agnostic and a social animal himself, he worked effectively with the religious and unsociable Faraday. He became friendly with Thomas Huxley and in 1856 they went to the Alps to study glaciers – as a consequence Tyndall became a noted 19th century alpinist after this visit and was first to climb the Weisshorn; he visited the Alps every summer from 1856 onwards and had a cottage at Belalp. His work on popularising science and his work on glaciers has meant that several geographical features were named after him including glaciers in Alaska, Colorado (*see picture on the front cover of this issue*), Chile and on Mount Kenya.

Whilst looking at glaciers and climbing mountains Tyndall wondered why there were glaciers all year round when the atmosphere could be very warm in the summer and as part of his investigations around this topic in the late 1850s and early 1860s he placed various gases in a tube and discovered that gases transmitted heat by different amounts,

"Remove for a single summer-night the aqueous vapour from the air which overspreads this country, and you would assuredly destroy every plant capable of being destroyed by a freezing temperature"

His work showed that very small quantities of gases like H_2O (and CO_2) can have a large influence on the temperature of the earth. Hence, although prior to Tyndall it was widely surmised that the Earth's atmosphere had a Greenhouse Effect he showed that water vapour was a strong absorber of heat and provided the first experimental evidence in support of it. [For further information, visit the American Institute of Physics: Center for History of Physics website**:** *Discovery of Global Warming* http://www.aip.org/history/climate/bibdate.htm].

The session after lunch commenced with **Professor Peter Brimblecombe** (UEA) whose topic was "The life and work of Arie Jan Haagen-Smit" which focused on boundary layer air pollution in Los Angeles. Urban air in the 20th century has been characterised by a transition from the presence of primary pollutants and reducing smog to an atmosphere where secondary pollutants and photochemical smog have become dominant. Professor Brimblecombe focused on Los Angeles as an exemplar of the phenomenon of photochemical smog and the attempts to resolve the problems associated with it. He characterised LA in the early 1940s as a city of 'vanishing streetcars' (portrayed as a failure of the public transport system) and a deliberate decision to turn LA into a motorised city. The consequences of this were immediate and in the 1940s air pollution was so bad that baseball games were no longer visible and, during WWII, the population feared the pollution was being generated by Japanese gas attacks – though the Southern Californian Gas Company's artificial rubber plant for butadiene was also considered as a possible source (albeit one which was protected because of its contribution to the war effort). But, even in the 1940s, there was an awareness that the LA smog was not a 'classical' smog but that it had a 'peculiar nature' - "LA has its own special brand of smog, less grim but more eye burning". Nevertheless, in spite of recognising that there was something different about LA smog, a Bureau of Smoke Control was established in 1945 and the LA administration apologised to the population for the problem saying it "would take a few months' to solve.

Professor Raymond Tucker (Chairman of the Engineering Department at Washington University) was invited from St Louis to help 'solve' the problem. His reputation was based on success in resolving pre-war issues with St Louis Smog, a problem associated with bituminous coal burning, and his comment that the automobile was definitely not the problem because there was so little sulfur in the petrol meant that little progress was made. Additionally it was also recognised that the association of the smog with a single source (i.e. the butadiene plant) which might have explained the 'peculiar' nature of the smog was an oversimplification.

Arie Jan Haagen-Smit (1900-1977) was a biochemist concerned with crop damage and had the skill of identifying components of the air by smell and was able to identify the presence of Criegee intermediates (products of ozonolysis) in the smog and hence say that it was caused by 'the action of sunlight and automotive vapours' and published his understanding of the nature of the smog in *Industrial & Engineering Chemistry* "The Chemistry and Physiology of LA Smog" (1952, **44**, 1342) referring to the presence of both ozone and peroxides. His ideas were opposed by the automobile manufacturers who commissioned a study at Stanford. The outcome of this study was broadly supportive of Haagen-Smit's approach though it was pointed out that more facts (reaction rates, reactive species etc.) needed to be known and, in the early 1970s, the hydroxyl radical was identified as an essential component of photochemical smog.

The story of LA Smog (and *inter alia* photochemical smog) is complex. The sources of the primary pollutants, their reactions, the role of the hydroxyl radical and the fact that there are multiple mobile polluters made understanding difficult and the development of policy *via* air quality management approaches was similarly difficult but it is remarkable that the nature of the smog only began to be unravelled when its smell was recognised by Haagen-Smit.

In the second presentation of the afternoon, "Robert Angus Smith and the search for wider and tighter pollution regulation," **Peter Reed** described the early stages of the development of Alkali Works legislation and how Smith's interpretation and application of the legislation established a *modus operandi* for 19th and early 20th century air pollution control in the UK.

In its initial stages (1863 legislation) the Alkali Inspectorate was chiefly directed at ensuring the capture of muriatic acid from the Leblanc process but over time (at Smith's behest) sulfur dioxide, sulfur waste, the copper industry (emissions of 'copper smoke' – sulphur dioxide and hydrogen fluoride), cement works (emissions of dust, volatile salts and a smell associated with the organic matter in the clay), potteries (smoke from coal and the release of hydrogen chloride when common salt was thrown over the pottery in the final stages of glazing) and ammonia emissions (from coal gas manufacture) were also included.

Although it was sometimes difficult (as when the Inspectorate was consistently refused permission to enter the Swansea Copper plant by the family who owned it), Smith persisted with the approach that persuasion was better than enforcement because the former allowed the Inspectors to act as peripatetic advisers rather than enforcers and this (usually!) produced more success and a better working relationship with the industry. Smith was also on favour of a high degree of central rather than local control – chiefly because it meant that he could have total oversight of the quality of analyses and the mode of implementation of the regulations.

The 1863 legislation had nothing to do with health but was focused on damage to property – the Act was heavily sponsored by the landed gentry in the House of Lords because it was their land that was being damaged by the emissions. However, prior to the 1863 Alkali Works legislation the 1848 Public Health Act had set up local Boards of Health and Medical Officers of Health in those areas where the death rate was greater than 23 per 1000 – at that time these deaths were chiefly associated with cholera, typhoid and smallpox. In terms of air pollution there were arguments that copper smoke was in fact a prophylactic against contagious diseases and Henry Vivian (who owned the Swansea copper works) gave workers dilute sulphuric acid to drink during a cholera outbreak. By and large noxious vapours were not considered to be injurious to health – workers in an atmosphere of hydrogen chloride protected themselves by breathing through piece of flannel. However, in the late 1890s Whitelegge (Chief Inspector of Factories) and Legge (Medical Inspector of Factories) began to look at industrial disease and thus the two strands of the inspectorate began to develop separate but linked agendas.

By 1956 the Alkali Inspectorate was responsible for 1900 processes and 1000 works in the UK and has subsequently become 'Her Majesty's Inspectorate of Pollution'. As such its responsibilities in relation to national air pollution management are those associated with industrial sources as opposed to the monitoring and management of other air pollution sources (such as cars) which are the responsibility of local authorities.

The penultimate talk of the meeting ("The life and work of Frederick Challenger") was delivered by **Professor Richard Bushby** (Leeds). Frederick Challenger (1887-1983) was the Professor of Organic Chemistry at the University of Leeds from 1930 to 1953 and in many ways his biography shows features which are recognisably those of scientists in the late 19th and early 20th century viz. he was born into a lower middle class family which embraced a work ethic, he studied in a provincial college and was sponsored by an academic 'patron', he showed flair as a researcher/experimentalist and then went (like Tyndall) to Germany for doctoral studies and after being awarded a PhD he came back to the UK to develop a successful career. (And, like Haagen-Smit, he had a great interest in smells; describing compounds as having 'butter-like' odours and 'the smell of a freshly opened corpse').

Challenger was born in the north of England (Halifax) and his father was a Methodist minister, he studied at Derby Technical College and in 1907 was awarded a London University External BSc in Chemistry. The Head of Chemistry at Derby (Jamieson Walker) encouraged him to apply for a job as a research assistant at Nottingham and whilst there Challenger published papers on organosilicon and organophosphorus and synthesised an optically active compound based on an asymmetric tetrahedral silicon atom. This work contributed to the award of an 1851 Exhibition Scholarship and he used this to go to Göttingen to work with the Nobel Laureate Otto Wallach on the terpenes thujone and thujaketonic acid – he also attended lectures on microbiological chemistry in Koch's laboratories. On his return to England in 1912 Challenger first worked as an assistant lecturer and demonstrator at Birmingham. There he became Acting Head in 1919 and was awarded his DSc in 1920. He moved to Manchester as a Senior Lecturer in 1920 and worked there until 1930 (in the same department as Robert Robinson). In 1930 Robinson's support for Challenger was sufficient for him to be appointed Head at Leeds in spite of the internal competition (J. W. Baker) sponsored by Christopher Ingold. His links to what is now known as Environmental Chemistry began in 1931 when he was asked to investigate the deaths of two children in the Forest of Dean which were attributed to Gosio Gas – the volatile form of arsenic formed by the action of fungi on arsenical green pigments used in wall paper and in clothing. Whatever the correctness of the identification of Gosio Gas as the killing agent, what is known is that Challenger successfully identified Gosio Gas as Me_3As rather than Et_2AsH which it was previously thought to be (*J. Chem. Soc.*, 1933, 95-101). Challenger extended this work to look at the function of the moulds *Scopulariopsis brevicaulis* and *Penicillium notatum* in the production of Me_2Se, Me_2Te and Me_3Sb by the unusual methylating agent which they contained (now known to be *S*-adenosylmethionine). This work on biological methylation is Challenger's major contribution to the field of environmental chemistry and has great ongoing importance for understanding the ways in which metals and metalloids are made bioavailable.

The final talk was given by **Chris Cooksey** on "The emergence of health concerns of the heavy metals and metalloids". This presentation focused on the development of LD_{50} as a measure of toxicity (J. W. Trevan, "The error of determination of toxicity" *Proc. Roy. Soc.*, 1927, **101B**, 483) and its subsequent translation into simple scales. [(Hodge and Sterner Scale – a 6-point scale ranging from extremely toxic ($LD_{50} \leq 1$) to relatively harmless ($LD_{50} > 15000$); the 4-point Globally Harmonized System of Classification and Labelling of Chemicals ($LD_{50} \leq 5$ 'Danger' to LD_{50} 300-2000 'Warning')]. Arsenic, mercury, lead and cadmium were then used as case studies to illustrate how awareness and knowledge of their effects developed over the later 19th and 20th centuries.

Arsenic's main use in the 19th century was as a pesticide ("Rough on Rats") – it was also known as 'inheritance powder'! More recently, during the Vietnam War arsenic containing compounds (sodium cacodylate and cacodylic acid – Agent Blue) were used as a 'rainbow herbicide' on rice paddies and other crops to deprive the Viet Cong of food crops. Arsenic poisoning kills by allosteric inhibition of essential metabolic enzymes, leading to death from multi-system organ failure – the more methylated the arsenic compound the less toxic it is (e.g. LD_{50} arsenate 112-175; LD_{50} dimethylarsinic acid 650). Trimethylarsine (Gosio Gas) has low toxicity chiefly because the process of inhalation limits its ingestion (The toxicity of trimethylarsine: an urban myth, *J. Environ. Monit.*, 2005, **7**, 11-15).

Mercury has been widely used (e.g. in Castner-Kellner Cells, for gold extraction, dental fillings, and measuring instruments). Peaks in the historical signature of mercury in the Fremont Glacier occur when volcanoes erupt (Tambora 1815, Krakatoa 1883, Mt St Helens 1980) and (because of its use to extract gold) during the periods of gold exploration (e.g. the 1850-1875 gold rush). Sixty-five percent of environmental mercury is from coal-fired power plants. Mercury has a long history of toxicity, and alkylation of mercury compounds in the environment (as occurred in Minamata) makes them more toxic. Currently dental fillings are the highest source of mercury exposure in Europe, and a fifty percent reduction in mercury emissions from crematoria by 2012 is demanded by EU legislation.

Lead poisoning causes 'colic', and beer standing overnight in lead pipes has been known to cause death (A Case of Lead Poisoning by Beer" E. R. Morgan, *British Medical Journal*, 1900, 1373). Lead, in its most recently ubiquitous tetraethyl form, has caused significant environmental damage which, since in the 1920s ten people died of insanity whilst working at the Ethyl Gasoline Company (which brought it to market), should have been signposted long before it was.

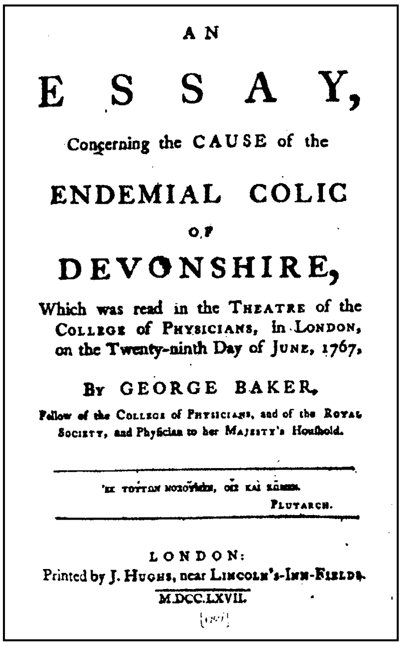
Cadmium was isolated in 1817 and the first report of poisoning was related to the cleaning of silver with cadmium carbonate in 1858. The most famous case of chronic poisoning occurred from around 1912 in the Toyama Prefecture of Japan due to cadmium extraction by the Mitsui Mining and Smelting Co and the consequent contamination of the Jinzu River. Since the river was used mainly for the irrigation rice fields cadmium accumulated in the people eating contaminated rice. Cadmium poisoning causes softening of the bones and kidney failure and the symptoms of intense pain from bone fractures and damage to joints and the spine gives its name (*itai-itai* – 'ouch ouch'). Production increased even more before WWII. The mines are still in operation and cadmium pollution levels remain high, although improved nutrition and medical care has reduced the occurrence of *itai-itai*.

The meeting was wide-ranging in its topics and gave a picture of some of the personalities and events responsible for the early stages in the development of environmental chemistry as a field of specialised study. It is noteworthy that knowledge and understanding of issues were gained from the personal enthusiasms and curiosity of highly skilled and highly motivated individuals; for the most part these were natural scientists, chemists, meteorologists and officers from local government and national agencies. Very few of them seemed to be driven by the exigencies of profit.

LEO SALTER

Chairman, RSC Environmental Chemistry Group

(Articles based on the proceedings of this meeting may be found on pp 9-28).



AN

ESSAY,

Concerning the CAUSE of the

ENDEMIAL COLIC

OF

DEVONSHIRE,

Which was read in the Theatre of the
College of Physicians, in London,
on the Twenty-ninth Day of June, 1767,

By GEORGE BAKER,

Fellow of the College of Physicians, and of the Royal
Society, and Phyſician to her Majesty's Houſhold.

[illegible]
Plutarch.

LONDON:
Printed by J. Hughs, near Lincoln's-Inn-Fields.
M.DCC.LXVII.
{1767}

In the 18th century, the use of lead containers for brewing cider was controversially suggested to be a cause of 'colic' in Devon. See – Waldron, H. A., Med. Hist.*, 1969,* ***13****, 74-81.*

Anthropogenic CO_2 and climate change – a historical perspective

Introduction

Climate is what we expect; weather is what we get. Thus, climate change is change in the type of weather we expect. In this article, I outline the development of our understanding of how changes to CO_2 levels and other greenhouse gases could affect climate. I first describe how climate change is observed, then how the understanding of CO_2 as a greenhouse gas arose in the late 1950's, before describing how climate is modelled. I finish with a short description of the evidence for a human influence on climate and what the future might hold. The material in this article is largely taken from Weart (2008), Edwards (2010), and Solomon *et al.* (2007). More details may be found in these three publications.

Observations of climate change

Observations of weather began in Europe in the late 17th century and had spread to most parts of the world by the 1950's. By the late 1930's G. S. Callendar (1898-1964), a British steam engineer, had compiled weather records, and claimed that the Earth was warming and this warming was being driven by CO_2 (Callendar, 1938). His claim was not really accepted at the time. In more recent work (for example Brohan *et al.*, 2006) many more land and marine observations, corrected for changes in observing practice and computed uncertainty estimates, have been compiled. These and other observational datasets (Solomon *et al.*, 2007) show ***unequivocal evidence*** of warming over the 20th century.

To extend climate records back prior to the instrumental period requires the use of proxies – biological or geological records of weather over a season or longer. For example, tree rings from carefully selected trees can record the average warmth of the growing season and so can be used to reconstruct climate. The modern instrumental record suggests that climate has warmed by about 0.8 K from 1900-2010 while uncertain proxy records of the last millennium suggest that the 20th century warming is unprecedented.

CO_2 as a greenhouse gas

Writing in the early 19th century, the French mathematician and physicist Jean Baptiste Joseph Fourier (1768-1830) suggested that the Earth was warmer than would be expected given the radiation from the sun. By the 1850's John Tyndall (1820-1893) had shown that water vapour, CO_2, and other gases absorbed infra-red radiation and were largely transparent to incoming solar radiation. In the late 19th century, Svante Arrhenius (1859-1927) proposed that CO_2 and other atmospheric gases caused the surface warming through their absorption of infra-red radiation, and he calculated how changes in CO_2 might warm the Earth's surface. However, CO_2 was seen as opaque and so increases in its concentrations would not affect climate as the "CO_2 effect" was saturated.

A group of scientists in 1950's California then tackled various aspects of the CO_2 problem. Gilbert Plass (1920-2004) (whose day job was researching infrared detectors for missiles) performed some calculations on the early computers to show that in the upper atmosphere CO_2 did not completely absorb infra-red radiation. This implies that changes in the concentration of atmospheric CO_2 could affect climate. Hans Suess (1909-1993) realised that fossil fuel carbon was depleted in ^{14}C as ^{14}C was produced in the atmosphere by cosmic ray bombardment and decays over a few tens of thousands of years. His early CO_2 measurements, using this ^{14}C-dating technique, suggested that most CO_2 emitted by fossil fuel burning would be taken up by the oceans and so would not affect climate. Oceanographer Roger Revelle (1909-1991) considered the chemistry of sea-water and found that it would take about a decade for the upper ocean to take up CO_2. But because of chemical buffering the upper ocean would then emit CO_2 back into the atmosphere. This implies that the upper ocean would not take up all the CO_2 emitted and some would end up in the atmosphere.

Charles Keeling (1928-2005) carried out the first direct and systematic measurements of carbon dioxide in the atmosphere at Mauna Loa, Hawaii in March 1958, and these measurements have continued, despite the foolishness of funding bodies, to this day. In his early work, Keeling showed that there had been a small but persistent increase in atmospheric CO_2 concentrations at the South Pole (Keeling, 1960). Since then the Mauna Loa record has found that annual average CO_2 concentrations increased from 316 ppm in 1959 to 390 ppm in 2010 (**Figure 1**).

By the early 1960's evidence indicated that when CO_2 is emitted into the atmosphere, the atmospheric concentration of this gas increases and could cause climate change. This led to the first report, in 1965, suggesting that CO_2 might be a problem, though it was considered unlikely that it would be a problem in the near future. Atmospheric concentrations of other greenhouse gases such as methane, nitrous oxide and the chlorofluorocarbons have also increased over the last 50 years.

As the Greenland and Antarctica ice-caps form, tiny bubbles of air are encapsulated within the ice. The contents of these bubbles can be analysed in ice core samples and tell us how atmospheric concentrations of greenhouse gases have changed over the last 800,000 years. Apparent in these records of past climates are the great swings associated with extensive northern hemisphere glaciations. At times of peak glaciation, atmospheric CO_2 levels are about 180 ppm while in inter-glacial periods, they reach values of about 280 ppm. By comparison, current atmospheric CO_2 and other greenhouse gas concentrations are unprecedented.

Modelling the global climate

In this section, I briefly outline two different approaches to modelling climate. The work described above had concluded that fossil fuel burning had the potential to affect climate but what was unclear was by how much. The amount of climate change depends on the "feedbacks" in the climate system. For example, water vapour is a greenhouse gas whose atmospheric concentration depends on the temperature. So if the temperature increases then the amount of water vapour in the atmosphere increases. This would then increase the greenhouse effect and thus the surface temperature. Early developments used *energy balance* models, which represented the fluxes of energy into and out of the Earth. The key ideas are that the outgoing energy flux depends on the greenhouse effect and the surface temperature. The effects of feedbacks are then represented through modifying the energy fluxes *via* a relationship with surface temperature.

The first attempt to numerically simulate the atmospheric flow for weather forecasting was made by L. F. Richardson (1881-1953), who carried out many of the calculations between ambulance shifts in the first world war (Richardson, 1922). Though the attempt failed, subsequent work built on Richardson's project. Following the second world war, electronic computers became available and numerical models of the atmosphere were developed. The first numerical simulations were carried out in the USA (Charney *et al.*, 1950). The UK Meteorological Office developed this USA work and instigated numerical methods in the early 1950's to forecast the weather using the LEO-1 computer (Lyons Electronic Office 1) (Bushby and Hinds, 1954). The Japanese meteorologist Syukuro Manabe (1931-), working at the Geophysical Fluid Dynamics Laboratory in the mid 1960's, was one of the first scientists to apply models of the atmosphere and ocean, which work by simulating flows using appropriate and approximate forms of the Navier-Stokes equations on a rotating Earth. One problem for these **General Circulation Models** (GCMs) is that many phenomena occur on scales which are not explicitly resolved and so their effects on the large-scale flow need to be parameterised. This parameterisation leads to uncertainty in climate prediction. Current GCMs simulate the atmospheric, oceanic and land surface flows on a grid of O(100x100) km. By the late 1970's two groups had constructed working GCMs, which included representations of the atmosphere, ocean and land-surface. The National Academy of Sciences commissioned a study on the possible effect of CO_2 on climate. This study reported that in response to the doubling of CO_2, the range of global-mean warming from the two models was 2-3.5 K with more warming at high latitudes. It also concluded, based on expert judgement, that the most probable warming in response to the doubling of CO_2 was 3 ± 1.5 K (Charney *et al.*, 1979). These figures were largely supported by Solomon *et al*. who concluded that it was *likely* that the response to the doubling of CO_2 was in the range 2.5-4.5 K (Solomon *et al.*, 2007).

Human influence on climate and future scenarios

Carrying out controlled experiments on the Earth's climate is not possible. However, by using GCMs with various different drivers one can compare these models with observations and determine the relative importance of human and natural drivers. Several different GCM's were constructed *either* with natural drivers *or* with *both* natural (changes in solar irradiance and volcanic effects) and human drivers (CO_2, other greenhouse gases and other human drivers). These models were then compared with observations of surface temperature change. Simulations with only natural drivers *were inconsistent* with the observations while those with natural and human drivers *were consistent* with observations. This work and other evidence led the IPCC to state *"Most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse concentrations"* (Solomon *et al.*, 2007).

Using GCM's, various modelling centres have simulated the possible response of the Earth's climate to different future emissions of CO_2 and other greenhouse gases. These different "scenarios" represent different future pathways of human development with no attempt to reduce CO_2 emissions to mitigate climate change. (Two examples are shown on p 36, based on Solomon *et al.*, 2007). Global-mean surface warming by 2100 is dependent on the choice of model and the scenario, but there is agreement that warming this century will warm the world to more than 2K above pre-industrial conditions – a level that the 2009 Copenhagen meeting deemed would represent dangerous climate change. In the scenario with the largest CO_2 emissions, models suggest that global-mean warming, relative to pre-industrial conditions, could reach 5K.

References

P. Brohan, J. Kennedy, I. Harris, S. F. B. Tett, and P. D. Jones (2006). Uncertainty estimates in regional and global observed temperature changes: a new dataset from 1850. *J. Geophys. Res.*, **111**, D12106.

F. H. Bushby and M. K. Hinds (1954). The computation of forecast charts by application of the Sawyer-Bushby two-parameter model. *Q. J. R. Meteorol. Soc.*, **80**, 165-173.

G. S. Callendar (1938). The artificial production of carbon dioxide. *Q. J. R. Meteorol. Soc.*, **64**, 223-240. (Available from http://www.rmets.org/pdf/qjcallender38.pdf).

J. G. Charney, R. Fjörtoft and J. von Neumann (1950). Numerical Integration of the Barotropic Vorticity Equation. *Tellus,* **2**, 237-254

J. G. Charney [+ co-workers] (1979). *Carbon Dioxide and Climate: A Scientific Assessment: Report of an Ad Hoc Study Group on Carbon Dioxide and Climate,* National Academies Press, Washington D.C.

P. N. Edwards (2010). *A Vast Machine: Computer Models, Climate Data, and the Politics of Global Warming*, MIT Press, Massachusetts.

C. Keeling (1960). The concentration and isotopic abundances of carbon dioxide in the atmosphere. *Tellus*, **12**, 200-203**.**

L. F. Richardson (1922). *Weather Prediction by Numerical Process*, Cambridge University Press, Cambridge.

S. Solomon [+ co-authors] (2007). *Climate Change 2007 – The Physical Science Basis.* Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge.

S. R. Weart (2008). *The Discovery of Global Warming*, (revised edn.), Harvard University Press, Cambridge, Massachusetts.

Other sources of historical information on climate change

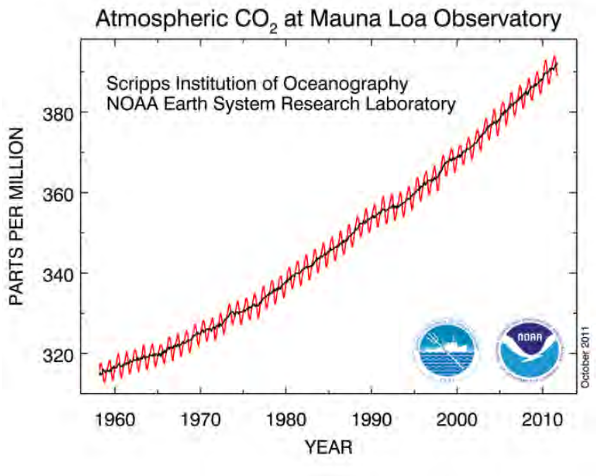
J. R. Fleming (1998). *Historical Perspectives on Climate Change*, OUP, New York.

Discovery of Global Warming http://www.aip.org/history/climate/bibdate.htm.

SIMON TETT

Chair of Earth System Dynamics &
Head of Global Change Research Institute,
School of Geosciences, University of Edinburgh,
Grant Institute, The King's Buildings,
West Mains Road, Edinburgh EH9 3JW
simon.tett@ed.ac.uk

This article is based on a presentation by Professor Tett at the joint ECG/Historical Group Symposium 'Environmental Chemistry: A Historical Perspective' *held at Burlington House on 26th October 2011.*



Now at about 390 ppm. In 1960 at about 310 ppm.

Airborne fraction about 0.5 mostly being taken up by terrestrial biosphere.

Figure 1: *Annual atmospheric CO_2 concentrations recorded at Mauna Loa, 1958-2010.*

Charles Keeling and the Mauna Loa Observatory, Hawaii

Held fast in the iron grip of frost: Field and laboratory in John Tyndall's discovery of the 'greenhouse effect'

John Tyndall was born on 2nd August 1820 at Leighlinbridge, County Carlow, Ireland, the son of a constable in the Royal Irish Constabulary. He attended the local National School and at the age of nineteen joined the Ordnance Survey of Ireland. Three years later, in 1842, he moved to the English Ordnance Survey in Lancashire where he worked until 1844 when he became a railway surveyor. In 1847 he was appointed to teach mathematics and surveying at Queenwood College, a school for boys in Hampshire. There he became friends with the chemistry teacher Edward Frankland (later Sir Edward Frankland an eminent Victorian chemist noted *inter alia* for his pioneering work in organometallic chemistry and valency theory).

In 1848 Tyndall (with Edward Frankland) moved to the University of Marburg in Hesse where he spent two intensive years studying chemistry, physics, and mathematics for the degree of Doctor of Philosophy. His teachers included the organic chemist Robert Bunsen, but the title for his doctorate thesis was a mathematical subject. With Bunsen's colleague, Karl Knoblauch, Tyndall began a series of studies on diamagnetism and the magneto-optical properties of crystals, phenomena that had been discovered by Michael Faraday in 1845. Tyndall continued this research when he went to Berlin in 1851 to work with Gustav Magnus.

These studies did not immediately produce a job in science, in either Germany or England, and so at the end of his time in Berlin he returned to Queenwood College. However, he began to be known in the English scientific community and at the 1851 Ipswich meeting of the British Association Tyndall met Thomas Huxley who became a lifelong friend. Furthermore he attracted the patronage of Henry Bence Jones, the Secretary of the Royal Institution, and Edward Sabine, the Treasurer of the Royal Society. After applying, unsuccessfully, for positions in various colonial universities, Tyndall was invited to delivered a Friday Evening Discourse at the Royal Institution in February 1853 which was so successful that in May he was appointed Professor of Natural Philosophy there. He thus became a colleague of Faraday's and, despite their differences in age and outlook, they became quite friendly, Tyndall looking up to him as a father figure – something that Faraday was slightly uncomfortable with.

Following a Friday Evening Discourse on the cleavage of slate in 1856 in which Tyndall argued that the phenomenon was caused by pressure alone, Huxley suggested that the same explanation might also account for the laminated structure of glaciers. Both Tyndall and Huxley then visited the Alps to study glaciers – it was the start of Tyndall's lifelong association with the Alps both as a subject of scientific study and as mountaineer. He was the first person to climb the Weisshorn in 1861 and seven years later became the first person to traverse the Matterhorn. Later he built a chalet at Belalp where he would spend much of the summers. During his first visit and thereafter annually, Tyndall, made many

John Tyndall in 1864 *(From a drawing by G. Richmond, R.A., at the Royal Institution)* measurements on glaciers and concluded that the motion of glaciers was due to the regelation of ice under pressure – a phenomenon that Faraday had discovered in the early 1850s.

While in the Alps, Tyndall observed the low temperatures in the mountains which he found strange because of the strength of the sun and the continuing existence of glaciers. This led him to research the part played by water vapour and other gases in absorbing and transmitting heat. Such studies had been undertaken previously for solids and liquids, but not for gases from which Tyndall concluded that the effect was probably small. During 1860 and 1861 Tyndall developed an experimental arrangement in the basement laboratory of the Royal Institution to measure heat transfer and absorption through gases. This involved the use of galvanometers and thermopiles to make measurements of heat passing through a long tube (**Figure 1**). He found that the main constituents of the atmosphere, nitrogen and oxygen, were almost entirely transparent to heat. However, and somewhat to his surprise, he observed that the smaller components of the atmosphere, for example carbon dioxide, water vapour or ozone absorbed more that 80% of the radiation passed through them. Tyndall explained this finding, as he sought to explain all natural phenomena, in terms of molecules. In this case compounds could vibrate in more ways than individual atoms.

Tyndall quickly recognized that although the quantity of gases such as carbon dioxide in the atmosphere was small, because of their very powerful absorptive properties, they exercised a disproportionate effect on the absorptive power of the atmosphere as a whole:

"Looking at the single atoms, for every 200 of oxygen and nitrogen there is about 1 of aqueous vapour. This 1, then, is 80 times more powerful that the 200; and hence, comparing a single atom of oxygen or nitrogen with a single atom of aqueous vapour, we may infer that the action of the latter is 16,000 times that of the former."

Thus a significant alteration in the quantity of water vapour or carbon dioxide would produce changes in the climate, and had probably happened in the past. As he put it:

"This aqueous vapour is a blanket more necessary to the vegetable life of England than clothing is to man. Remove for a single summer-night the aqueous vapour from the air which overspreads this country, and you would assuredly destroy every plant capable of being destroyed by a freezing temperature. The warmth of our fields and gardens would pour itself unrequited into space, and the sun would rise upon an island held fast in the iron grip of frost."

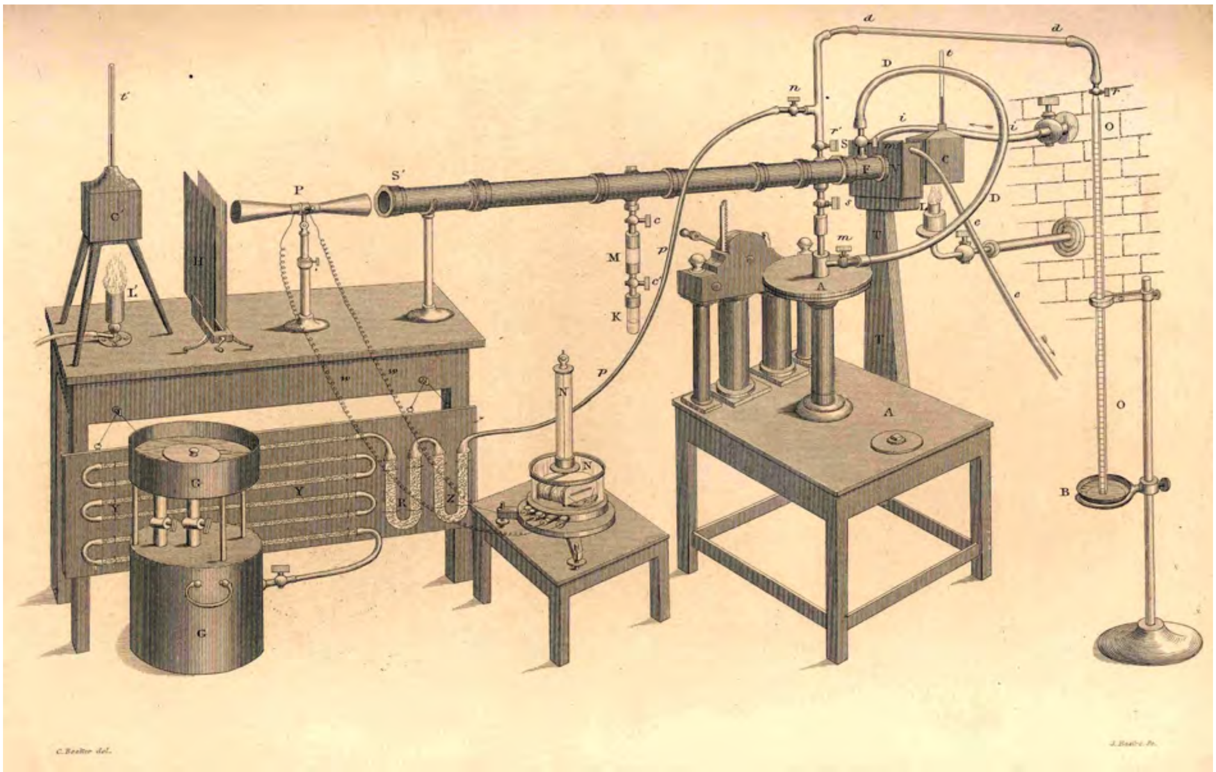


Figure 1: *The first ratio spectrophotometer, assembled by John Tyndall, which he used at the Royal Institution from 1859 onwards to study the absorption of radiation by gases and vapours.*

The memorial stone to John Tyndall at Belalp, Valais, Switzerland

> *" … the aqueous vapour of the atmosphere must act powerfully in intercepting terrestrial radiation; its changes in quantity would produce corresponding changes of climate. Subsequent researches must decide whether this* vera causa *is competent to account for the climatal changes which geologic researches reveal."*
>
> John Tyndall, *Proceedings of the Royal Society of London*, 1860-1862, **11**, pp 100-104.

Shorn of Tyndall's insularity, this is a description of the 'greenhouse effect', which is now recognised as one of the major drivers of global climate change.

Although Tyndall carried out the fundamental physics and chemistry in the Royal Institution's laboratory, the initial idea for this research came from his time in the field, amongst the mountains and glaciers of the Alps. It is in the latter aspect that Tyndall's contribution has been publicly recognised by the naming of mountains and glaciers after him around the world. These and other glaciers are now in retreat, and it is to be hoped that by continued understanding of the mechanisms involved, initiated by Tyndall's research, and taking the appropriate social, economic and political actions, that the glaciers named after him will continue to exist long into the future.

FRANK A. J. L. JAMES

Royal Institution,
21 Albemarle Street,
London, W1S 4BS
fjames@ri.ac.uk

Further reading

1. A. S. Eve and C. H. Creasey, *Life and Work of John Tyndall*, Macmillan & Co., London, 1945.
2. N. D. McMillan, R. C. Mollan and W. H. Brock (editors), *John Tyndall: Essays on a Natural Philosopher*, Royal Dublin Society, Dublin, 1981.
3. J. R. Fleming, *Historical Perspectives on Climate Change*, Oxford University Press, New York, 1998.
4. W. H. Brock, 'Tyndall, John (1820-1893)', *Oxford Dictionary of National Biography*, Oxford University Press, Oxford, 2004.

This article is based on a presentation by Professor James at the joint ECG/Historical Group Symposium 'Environmental Chemistry: A Historical Perspective' *held at Burlington House on 26th October 2011.*

Arie Jan Haagen-Smit and the history of smog

Air pollution in the 20th century was characterised by a transition from urban air dominated by primary pollutants to one where secondary pollutants became more important. These newer pollutants involved chemical reactions and species that were not easy to unravel compared with those from combustion sources. One of the first urban environments where this shift to secondary sources of air pollution was recognised was Los Angeles.

Los Angeles grew through the early 20th century. Initially the city had a network of electric streetcars known as The Los Angeles Railway, but this was gradually eroded after being sold to companies with interests in other modes of transport. This conspiracy is often called "The Great American Streetcar Scandal" in which General Motors (GM) and other companies undermined the provision of streetcar services. The consequence was the dominance of automobiles and hydrocarbon combustion for mass transportation.

Los Angeles smog began to be apparent in the early 1940s, but initial attempts to identify the source of the smog were unsuccessful. Some people blamed the Southern California Gas Company's artificial rubber plant which used butadiene, but the complaint was muted because of the strategic importance of rubber to the war effort. Butadiene is highly reactive, and may have been a localised source of smog, but it was probably not entirely to blame because even when the plant was shut down, the smog continued (Dunsby, 2003).

Although the word smog (Smoke + fOG) was chosen to describe the air pollution of Los Angeles it contained neither smoke nor fog. However, even in the 1940s there was an awareness of the "peculiar nature" (Krier and Ursin, 1977). Despite an absence of smoke, ironically Los Angeles set up a Bureau of Smoke Control in 1945. After the war smog continued to be a serious problem, and the *Los Angeles Times* invited Raymond Tucker, a pollution expert from St Louis, to investigate the smog. He had been successful in solving Pittsburgh's smoke problems, so seemed a good choice. Tucker argued that the automobile was not really the cause as there was virtually no sulfur in the fuel. This failed to recognise that Los Angeles smog was something entirely new.

As in London, where the Victorian smogs became indelibly associated with the growth of detective fiction (from Sherlock Holmes onwards), Los Angeles was birthplace of the hard-boiled detective (Brimblecombe, 1990). Smog appears frequently although in the archetypical Philip Marlowe stories of Raymond Chandler smog is not really described in detail until *The Long Goodbye* of 1953. In other Hollywood fiction, smog came to represent a kind of explanation of evil intent:

> *"...in the hot glow of an August morning. The smog was already coalescing into a solid sheet, burying the Hollywood Hills in a blinding pall that would remain for weeks as the foul summer air compressed itself into a burden on the lungs, the mind and the human heart."*

Mary Lawrence Gregory, *Equal to Princes*, Doubleday, 1986.

Los Angeles Ry 3 at Los Angeles, CA

Don Ross Collection

Los Angeles streetcar *ca.* 1917

Cutting a metaphorical knife through the Los Angeles smog and its fictional manifestations came the scientific reasoning of the Dutch-born natural product chemist and biochemist, **Arie Jan Haagen-Smit**.

Arie Jan Haagen-Smit was born in Utrecht in 1900 and completed his PhD studies at the University of Utrecht in 1929 with an investigation of some sesquiterpenes under the supervision of Leopold Ruzicka, from whom he acquired a life-long interest in terpenoids – from isoprene to polyterpenes (e.g. rubber). Haagen-Smit carried out pioneering work in Utrecht on plant growth hormones before settling in California in 1937. At Caltech, he resumed his work on terpenes by identifying their presence in food flavours. In the late 1940's Haagen-Smit became concerned about crop damage and the impact of the Los Angeles smog. He thought that the city's air seemed to smell like an organic chemistry laboratory, perhaps indicative of Criegee ozonolysis intermediates, which suggested the action of ozone on unsaturated organic molecules. There was no source for ozone, so this had to be produced in the atmosphere as a secondary pollutant. Haagen-Smit determined that the Los Angeles smog arose through the action of sunlight in the presence of automotive vapours.

The early research highlighted that smog is not only injurious to health but it also damages materials such as rubber. Haagen-Smit had devised a simple test for the presence of ozone in air by observing the deterioration of 'bent' (i.e. stressed) rubber tubing (polyisoprene) in an air sample. Smog is also a lachrymator – later ascribed to the presence of peroxyacetyl nitrate. Haagen-Smit published his work on the origins of Los Angeles smog in the early 1950's (e.g. Haagen-Smit, 1952; Haagen-Smit *et al.*, 1953) where he referred to both ozone and peroxides in the atmosphere. Perhaps more importantly he realised the policy implications and wrote: "a proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emissions, but also their fate in air". He also contributed to popular articles in magazines such as *Life* and *Scientific American* where he wrote: "the Los Angeles atmosphere differs radically from that of most other heavily polluted communities" (Haagen-Smit, 1964). His picture of the smog was relatively simple, but was opposed by the automobile manufacturers and the oil companies. They sponsored research by the Stanford Research Institute, which ultimately confirmed the role of automotive fuel in creating the smog.

Our modern understanding of smog chemistry derives from photochemist Philip Albert Leighton's book *Photochemistry of Air Pollution* (1961). In a book review, the eminent physical chemist Henry Eyring quoted Leighton: "a major share of the photochemically originated organic particulates in photochemical smog are due to the nitrogen dioxide-olefin photolysis and the reactions which follow", (Eyring, 1962). However, Eyring was not entirely convinced this was the complete story and believed that "many features will undoubtedly be modified and amplified with time." Another reviewer Morris Katz realised the regulatory significance of the chemistry: "in order to control such harmful by products… [we need to] know the facts concerning their formation and reactions" (Katz, 1961).

Arie Jan Haagen-Smit (1900-1977)

We now know that hydroxyl radicals play a pivotal role in the formation of smog. Altshuller and Bufalini (1971) consider that our current understanding of smog emerged in the late 1960s. Stern's *Air Pollution*, 2nd edition, 1967-1968 mentions peroxides but not a role for the hydroxyl radical in smog formation. Hiram Levy II (1971) identified the hydroxyl radical as a basic ingredient for the production of photochemical smog. Reactions of OH with CO were also appreciated to be significant (Westberg and Cohen, 1969). A lack of a clear understanding of smog chemistry and the importance of the reactivity of individual hydrocarbons meant that a number of mistakes were made in finding solutions to air pollution problems, perhaps most notably in Mexico City in the 1980s.

Problems posed by smog – scientific, legislative, and financial – have proved difficult to solve, but chemistry has contributed to the way air quality is managed in a world where air pollution issues have become more complex. This has meant that a careful approach to regulation has achieved impressive results (Parrish *et al.*, 2011). It is important to note that Arie Jan Haagen-Smit, who recognised the origin of the smog, also addressed the implications that smog has for policy, showing that good chemists are not as removed from the world around them as some detractors might imagine.

References

Altshuller, A. P. and Bufalini, J. J. (1971). Photochemical aspects of air pollution: A review. *Environmental Science and Technology*, **5**, 39-64.

Brimblecombe, P. (1990). Writing on smoke. In: H. Bradby (Editor), *Dirty Words,* Earthscan Publications Ltd., London, pp 93-114.

Dunsby, J. (2003). Localizing smog: transgressions in the therapeutic landscape. In: M. De Puis (Editor), *Smoke and Mirrors*, University of New York Press, NY, pp 170-200.

Eyring, H. (1962). Sunlight and health hazards. *Science*, 9th February, 427-428.

Haagen-Smit, A. J. (1952). The chemistry and physiology of Los Angeles smog. *Industrial & Engineering Chemistry*, **44**, 1342-1346.

Haagen-Smit, A. J. (1964). The control of air pollution. *Scientific American*, **210**, 25-31.

Haagen-Smit, A. J., Bradley, C.E. and Fox, M.M. (1953). Ozone formation and the photochemical oxidation of organic substances. *Industrial & Engineering Chemistry*, **45**, 2086-2089.

Katz, M. (1961). Some aspects of the physical and chemical nature of air pollution. *Air Pollution*, World Health Organisation, Geneva, pp 97-158.

Krier, J. E. and Ursin, E. (1977). *Pollution and Policy*, University of California Press, Berkeley and Los Angeles.

Levy II, H. (1971). Normal atmosphere: Large radical and formaldehyde concentrations predicted. *Science*, **173**, 9th July, pp 141-143.

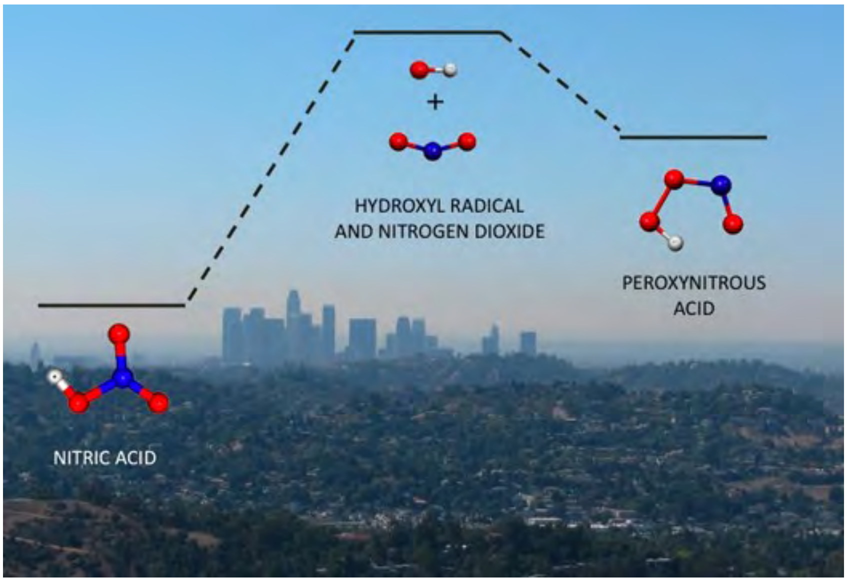
Parrish, D.D., Singh, H.B., Molina, L. and Madronich, S. (2011). Air quality progress in North American megacities: A review. *Atmospheric Environment*, **45**, 7015-7025.

Westberg, K. and Cohen, N. (1969). The chemical kinetics of photochemical smog as analyzed by computer, Report ATR-70-(8107), Aerospace Corp, El Segundo, California.

PETER BRIMBLECOMBE

School of Environmental Sciences,
University of East Anglia,
Norwich NR4 7TJ, UK

This article is based on a presentation by Professor Brimblecombe at the joint ECG/Historical Group Symposium ‘Environmental Chemistry: A Historical Perspective’ *held at Burlington House on 26th October 2011.*



Nitrogen dioxide and the hydroxyl radical combine in the atmosphere (e.g. Los Angeles) to make either nitric acid or peroxynitrous acid; the so-called branching ratio of these two chemicals is important in models of ozone production, and influences smog formation. Mollner, A. K.; Bloss, W. J. et al., Science*, 2010,* ***330****, 646.*

Robert Angus Smith and the pressure for wider and tighter pollution regulation

Born into an intensely religious family in Pollokshaws, near Glasgow, in 1817, Robert Angus Smith became interested in chemistry through attending lectures in the late-1820s given by Thomas Graham (one of the founders of the Chemical Society of London). Smith completed his chemical education by obtaining a PhD under the tutelage of Justus von Liebig at the University of Giessen in 1841. A fellow student at Giessen, Lyon Playfair, invited Smith to become his assistant at the Royal Manchester Institution in 1843, and the two men collaborated on a report on sanitary conditions in industrial Lancashire, and in particular on the role of decomposing matter in disease (which was also one of Liebig's interests). Playfair left Manchester in 1845, but Smith remained and became a successful consulting analytical chemist with many friends and colleagues in the heavy chemicals industry of northern England. Through these friendships, Smith became aware of the distortion of evidence in several cases where chemists had been summoned as expert witnesses in legal actions brought against chemical companies accused of pollution offences. Smith began a campaign for the reform of scientific testimony in courts of law and later was joined by William Crookes and *Chemical News*, *The Times*, *Nature* and the British Association for the Advancement of Science. While in Manchester Smith had begun to study air quality, reporting to a number of Parliamentary enquiries. When the Alkali Works Act of 1863 was passed, Robert Angus Smith was an obvious candidate for the post of Inspector.

Parliament approved the Alkali Works Act for an initial 5-year period to regulate the release of hydrogen chloride gas (or muriatic acid gas, as it was called in the alkali trade) by alkali works operating the Leblanc process. Under the Act the Alkali Inspectorate was established and a team of four sub-inspectors under Smith as Inspector ensured at least 95% of the corrosive gas was condensed and not released from tall chimneys. Many promoted this noxious vapour for its prophylactic benefits. The Act was extended indefinitely in 1868 and then revised in 1874 with a volumetric measure for measuring gas escapes; sulfur dioxide and nitrogen dioxide emissions were also regulated.

The remainder of the 19th-century brought dramatic increases in both the tonnages of chemicals produced and the range of nuisances from chemical processes. Robert Angus Smith (supported by his inspectors) used every opportunity to draw attention to these unregulated nuisances whether in his Annual Reports to Parliament, through discussion within the Local Government Board or during Parliamentary enquiries such as the 1876 Royal Commission on Noxious Vapours.

These unregulated nuisances included sulfur waste, copper works (in the main Swansea and St Helens), cement works, potteries (particularly salt-glaze) and ammonia. Sulfur waste was produced during the third stage of the Leblanc process and by the 1870s some 500,000 tons of waste were produced annually in Britain since between 1.5 and 2 tons of waste resulted from every ton of soda produced. This waste contained almost all the sulfur originating from the sulfuric acid in the first stage. Given that sulfur was expensive and regular supplies (initially from Sicily) were difficult to secure, some attempts were made to recycle the sulfur (Gossage in 1837; Mond in 1861; McTear in 1871) but these proved unsuccessful on the large-scale (until the Claus-Chance process in 1881) and most waste was dumped on waste ground surrounding the alkali works. The waste proved to be a constant source of sulfur dioxide and hydrogen sulfide pollution.

Robert Angus Smith (1817-1884)

Copper works in Swansea and St Helens were regular polluters. The smoke comprised a concentrated mix of the gases sulfur dioxide and hydrogen fluoride with particles of copper, sulfur, arsenic, lead, antimony and silver. Estimates in the 1840s indicate the Swansea smelters released about 92,000 tons of sulphurous acid. Ammonia was an infrequent polluter but any release caused a major hazard. Most ammonia came from gas works and it was generally during transportation of the ammonia liquor to fertilizer works for conversion into ammonium sulfate that dangerous incidents (sometimes resulting in death) were reported.

Portland cement works were regularly reported to the Inspectorate and offending nuisances included dust, volatile salts of potassium chloride, sodium sulfate and potassium sulfate and a smell originating from the organic matter in the clay. Although furnaces were redesigned regularly the dust remained a problem well into the 20th-century. Potteries were also brought to the attention of the Inspectorate, largely because of black smoke from burning coal for heating the kilns; on many occasions the atmosphere of Longton was likened to that of Widnes. However, salt-glaze potteries were singled out for particular attention because during the final twenty-minutes of firing common salt was thrown over the red-hot pottery with the release of hydrogen chloride gas.

Changes to the regulatory framework were adopted from the 1870s to strengthen the powers of an Alkali Inspectorate facing an ever-increasing list of nuisances. These included "best practicable means", continuation of central regulation, enforcement by legal prosecution and swifter regulation of nuisances. Smith and his inspectors had developed a stance on manufacturers adopting the "best practicable means" for preventing the discharge of pollutants into the atmosphere. In many cases the technical means for remaining within desirable limits were not available and yet by adopting the "best practicable means" and working closely with the inspectors manufacturers were more likely to develop the technical solution. This approach was also supported by manufacturers.

The benefit of central regulation rather than delegation to local authorities was a constant point of debate following the transfer of the Alkali Inspectorate to the Local Government Board in1872 as part of the Public Health Act. The Board was adamant the Inspectorate should be devolved but Smith fought hard for central regulation – consistency of regulation, well-qualified and experienced staff, cost-effective administration and independence from local vested interests. The debate came to a head during the Royal Commission on Noxious Vapours (1876) and its Report in 1878 supported Smith's position.

However, Smith had to bow to pressure from the Board over enforcement by legal prosecution. Following his traumatic experience as a defence witness in the Peter Spence court case in 1857, Smith had fought long and hard to adopt a co-operative approach with manufacturers whereby inspectors acted as peripatetic consultants and avoided using the courts. In the lead up to the 1876 Royal Commission Smith was asked how many prosecutions had been taken out; his reply was four. This appalled his civil service colleagues given the extensive damage cited when legislation was being drawn up in 1863. After 1878 Smith was instructed to use the courts for enforcement but remaining reluctant he always made sure the final decision was taken in consultation with the Local Government Board so as not to undermine his relationship with manufacturers.

With the increasing notification of nuisances it became important to have a mechanism whereby nuisances could be added to the "regulated list" quite quickly and not have to wait until a Parliamentary enquiry produced a report. Following from the recommendations of the 1876 Royal Commission on Noxious Vapours, revised legislation in 1881 gave powers to the appropriate minister to make Orders extending the list of scheduled processes and noxious and offending gases.

The impact of these nuisances on public health and occupational health began to be studied seriously from the 1870s. Before this the prophylactic benefits of the nuisance vapours were often promoted; Henry Hussey Vivian was so convinced of the benefits of sulphurous copper smoke from his smelters that he gave his workers dilute sulfuric acid to drink during a cholera outbreak! Even Medical Officers of Health (appointed from 1848) found difficulty apportioning responsibility to nuisance vapours for illness and death. John Simon, Medical Officer to the Local Government Board, was however adamant about the blight caused to people's lives by these toxic vapours.

The public and manufacturers were often ignorant of the long-term effects of industrial work on health. The 1895 Factory and Workshop Act required the notification of industrial diseases for the first time, including lead, arsenic and phosphorus, but it was only with the appointment of Dr Arthur Whitelegge as Chief Inspector of Factories in 1896 and Thomas Legge as the first Medical Inspector of Factories in 1898 that a concerted effort began against industrial disease.

[An article covering the main topics in this talk will be published in the July 2012 edition of *Ambix* in a special volume commemorating the publication of Rachel Carson's *Silent Spring* in 1962].

PETER REED
peter@peternreed.plus.com

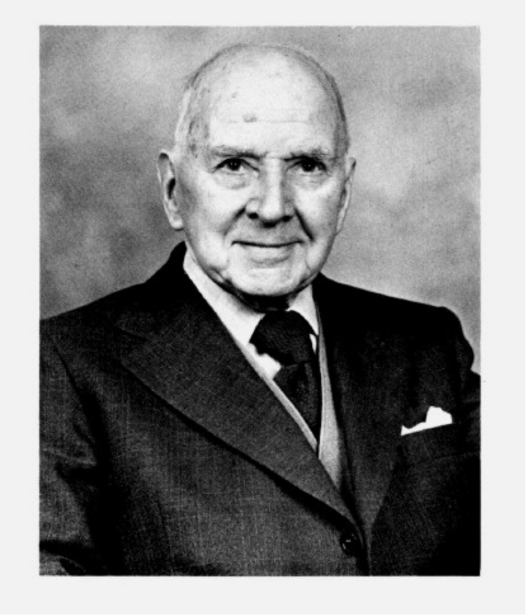
Further reading

C. Hamlin, 'Smith, (Robert) Angus (1817-1884)', *Oxford Dictionary of National Biography*, (Oxford: Oxford University Press, 2004).

This article is based on a presentation by Peter Reed at the joint ECG/Historical Group Symposium 'Environmental Chemistry: A Historical Perspective' *held at Burlington House on 26th October 2011.*

The life and work of Frederick Challenger

Fred Challenger had a long and distinguished career touching on many areas of organic and organometallic chemistry, but these days he is chiefly remembered for his work on biomethylation. He retired as Professor of Organic Chemistry at Leeds University in 1953, but was still actively engaged in research when I arrived as a junior lecturer at Leeds in 1970, so I got to know him quite well. He published his last paper at the age of 91 (1978) and gave his last public lecture only a matter of weeks before he died in 1983.

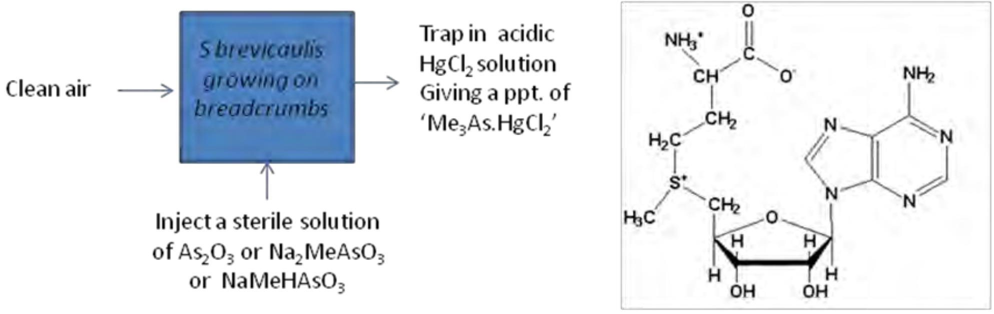


Frederick Challenger (1887-1983)

After a rather unpromising start (he obtained a third class London external degree in Chemistry from Derby Technical College), Challenger obtained a position with F. S. Kipping at University College Nottingham (1907-1910). Here he flourished, succeeding in making and resolving the first optically active compound based on an asymmetric silicon atom. For this work Challenger was awarded a prestigious '1851 Exhibition' Scholarship which gave him the financial resources he needed to continue his chemical studies in Germany. He arrived in Göttingen to work with Otto Wallach in 1910, the same year that Wallach was awarded the Nobel Prize. His PhD (1910-1912) was concerned with straightforward terpene chemistry, but it was in Göttingen that he began to develop an interest in microbiological transformations – mainly through the influence of the Professor of Agricultural Bacteriology, Alfred Koch. Subsequent appointments as a lecturer in Birmingham (1912-1920) under P. F. Frankland and as a senior lecturer in Manchester (1920-1930) under Robinson and Lapworth were followed by Challenger's appointment to the Chair of Organic Chemistry at the Leeds University in 1930 where he succeeded C. K. Ingold.

At Leeds one of the first scientific problems Challenger tackled was the nature of 'Gosio gas' – a volatile toxin thought at that time to be produced in damp rooms from wallpapers and fabrics coloured with arsenical pigments, and named after the Italian physician Bartolomeo Gosio. Challenger's interest was sparked by an alleged case of Gosio gas poisoning in the Forest of Dean in which two children had died. It was the beginning of a fascination with the process of decay, the microbiological transformations that are involved in decay, and particularly the (often bad) smells that are given off. [Whether a toxic gas was actually produced from arsenical pigments under the conditions described has been questioned by Cullen and Bentley (2005). Challenger's identification of trimethylarsine as a microbial metabolite of inorganic arsenic is not disputed].

The general approach adopted in many of these experiments is shown in the **Scheme 1**. Cleaned air was passed over a culture of mould grown on breadcrumbs and a sterile solution of an inorganic arsenic compound was injected. Once the foul smell of Gosio gas was detected in the effluent gas, this was passed through an acidic solution of mercuric chloride. The precipitate formed was identified as '$Me_3As.HgCl_2$' showing Gosio gas to be trimethylarsine and not, as had previously been thought, diethylarsine. Interestingly, these moulds were also shown to have the ability to methylate inorganic antimony, selenium and tellurium compounds – essentially removing these toxic elements from their environments by converting them into volatile derivatives. The long struggle to understand the mechanism of biomethylation culminated in the early 1950's when Challenger and his co-workers demonstrated that the methyl group is derived from *S*-adenosylmethionine. Challenger's mechanism for the biomethylation of metalloids and, in particular, the conversion of arsenate into trimethylarsine – a sequence of four two-electron reductions and three methyl group transfers – is commemorated as the 'Challenger Pathway' **(Scheme 2)**.



In a similar manner and using *S. brevicaulis, Penicillium notatum*, etc. Na_2SeO_3 or $NaMeSeO_2$ gave Me_2Se (*J. Chem. Soc.*, 1934, 68; *J. Chem. Soc.*, 1942, 574); K_2TeO_3 gave Me_2Te (*J. Chem. Soc.*, 1939, 574); Various antimony compounds such as H_3SbO_4 gave Me_3Sb (*Barnard thesis*, Leeds 1937)

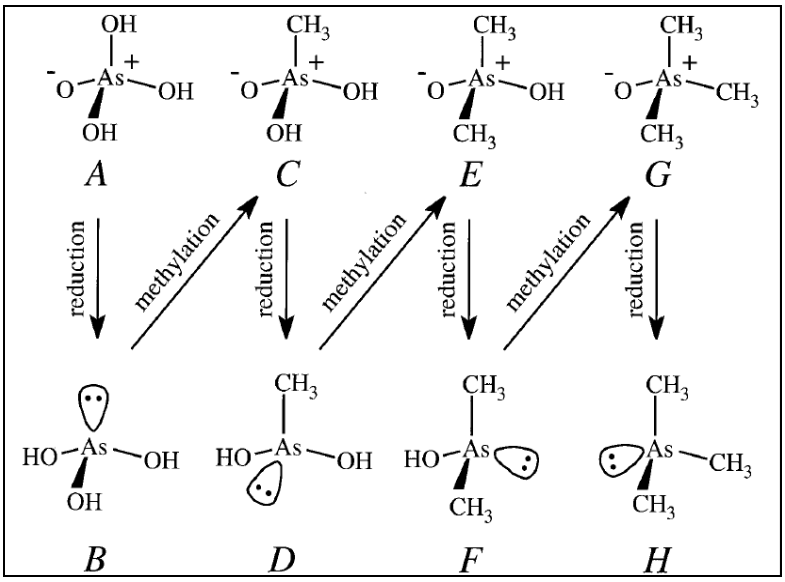
Scheme 1: Top left – *experimental approach to studying biomethylation;*
Top right – *Formula of the general biological methylating agent S-adenosylmethionine*

Biomethylation has important implications for the toxicity of metals and metalloids and for their distribution in the environment.

Two themes run through almost all of Challenger's work: a human interest and a fascination with the way organic compounds smell. These led him into all sorts of other areas including an interest in volatile compounds from rocks, from shale and from rotting seaweed and studies of medical conditions involving patients who developed foul-smelling urine or foul-smelling breath. Challenger's involvement in tellurium metabolism illustrates the way human stories often attracted his attention. He was fascinated that students working in the Inorganic Chemistry Section at Leeds under Professor Whitelaw-Gray, who were making tellurium compounds, rapidly developed extremely bad breath even though they had not been exposed to volatile tellurium compounds! Clearly the human body is very efficient at processing inorganic tellurium into a volatile derivative: in this case Me_2Te.

Frederick Challenger is remembered by his colleagues at Leeds for running an exceptionally harmonious Organic Chemistry Department, by local schools for his talks and exciting lecture demonstrations (some of which would certainly be banned by health and safety regulations today), and by those of us who knew him personally as a gracious and kindly man who had a genuine interest in young members of staff and a real desire to see them succeed.

If anything, his scientific reputation has grown with the passage of the years. In his day the environmentally-related problems in which he was interested were not very highly regarded by the UK's organic chemistry establishment, indicated, perhaps, by Challenger's exclusion from election to the Royal Society of London.



Scheme 2: *Challenger Pathway for the conversion of arsenate (A) into trimethylarsine (H)*

Further reading

1. ‘Frederick Challenger 1887-1983: chemist and biochemist’, T. G. Chasteen and R. Bentley, *Appl. Organomet. Chem.*, 2003, **17**, 201.
2. ‘The Chemistry Department of the University of Leeds’, F. Challenger, *J. R. Inst. Chem.*, April 1953.
3. ‘Biological methylation’, F. Challenger, *Q. Rev., Chem. Soc.*, 1955, **9**, 255.
4. Archive Material from the University of Leeds, the University of Leeds Department of Chemistry, the RSC, and Ashville College Harrogate.
5. ‘Microbial methylation of metalloids: arsenic, antimony, and bismuth’, R. Bentley and T. G. Chasteen, *Microbiol. Mol. Biol. Rev.*, 2002, **66**(2), 250.
6. ‘Methyl mercaptan in relation to foetor hepaticus’, F. Challenger and J. M. Walshe, *Biochem. J.*, 1955, **59**(3), 372.
7. ‘The toxicity of trimethylarsine: an urban myth’, W. R. Cullen and R. Bentley, *J. Environ. Monit.*, 2005, **7**, 11.

Acknowledgements: Thanks for help with archive material to Joanne Fitton, Rupert Purchase, Mike Burke and Don Grayson

RICHARD J. BUSHBY

Centre for Molecular Nanoscience (CMNS)
University of Leeds LS2 9JT

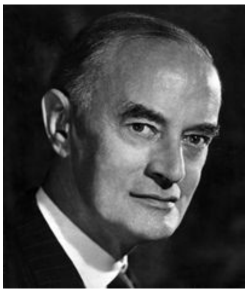
This article is based on a presentation by Professor Bushby at the joint ECG/Historical Group Symposium ‘Environmental Chemistry: A Historical Perspective’ *held at Burlington House on 26th October 2011.*

University of Leeds Chemistry Department

Department part of the ‘Baines Wing’ 1908-1933

New (present) Building 1933-

J B Cohen 1904-1924



C K Ingold 1924-1930

F S Challenger 1930-1953

Heads of the University of Leeds Chemistry Department in the first half of the 20th century

Health concerns of heavy metals and metalloids

There is a long history and an overwhelming amount of data on the toxicity of heavy metal compounds. Here we take a brief look at some aspects of the toxicity of **arsenic**, **mercury**, **lead** and **cadmium**, and highlight the contrast between the acute and chronic toxicity of purely inorganic metal and metalloid species and their organometallic derivatives.

Acute and chronic toxicity

Sometimes the distinction between acute toxicity and chronic toxicity is not very clear, but generally acute toxicity is the result of a single exposure leading to illness or death, whereas chronic toxicity is the result of long-term exposure leading to illness or death. A measure of acute toxicity was originally developed to test the strength of pharmaceutical preparations which could not be measured by chemical means, for example, digitalis. Fox glove preparations have been used medically since the 18th century, sometimes with dire consequences because the concentration of the active principle, digitalis, depends on the quality of the plant and the efficacy of the extraction process. The difference between the dose required for a medical effect and that which could prove fatal is not large. A measure of the acute toxicity of pharmaceutical preparations was devised by Dr. John William Trevan (1887-1956) a pharmacologist who was director of the Wellcome Research Laboratories until he retired in 1953. In this test, a number of rats were given various single doses of the test material and from the number who died within a day or two a figure of the median lethal dose, LD_{50}, could be determined.[1] Typical values for LD_{50} are given in **Table 1**.

	LD_{50} (rat, oral) mg/kg
CdS	7080
NaCl	3000
As	763
HgCl	210
NaF	52
Tl_2SO_4	16
NaCN	6.4
$HgCl_2$	1

Table 1: *Typical LD_{50} values for rats.*

It may be a surprise that cadmium sulfide is less toxic than sodium chloride, but that is only due to its low solubility; more noteworthy is that mercury(I) compounds are two hundred times less toxic than mercury(II) compounds. Some idea of the human toxicity of the compounds in the list can be can be gained by multiplying the LD_{50} value by the weight of a standard adult male, 60 kg in the EU or 80 kg in the USA.

For many years it was customary to convert the numbers into words, using the Hodge and Sterner Scale (1949), which could then be used on labels (**Table 2**):[2]

Toxicity Rating	Commonly used term	LD_{50} (rat, oral) mg/kg
1	Extremely Toxic	<=1
2	Highly Toxic	1 - 50
3	Moderately Toxic	50 - 500
4	Slightly Toxic	500 - 5000
5	Practically Non-toxic	5000 - 15000
6	Relatively Harmless	>15000

Table 2: *Hodge and Sterner Scale.*

This has been replaced, in Europe, by the Globally Harmonised System of Classification and Labelling and Packaging of Chemicals, which is much simpler (**Table 3**):[3]

Toxicity Rating	**Words used**	**LD_{50} (rat, oral) mg/kg**
1	Danger	<=5
2	Danger	5 - 50
3	Danger	50 - 300
4	Warning	300 - 2000

Table 3: *Globally harmonised system*.

Arsenic

Arsenic has been known from antiquity to be toxic and is popularly associated with accidental or deliberate poisoning leading to death. It was widely available until the mid-20th century and was used as a pesticide against rats but is now replaced by thallium salts or Warfarin. The use of arsenic, as the oxide, in taxidermy to preserve specimens from insect attack was introduced by Jean-Baptiste Bécoeur (1718-1777) and was in use in museums until the 1980s.[4] A related use of arsenic compounds is as a herbicide: Agent Blue was one of the rainbow herbicides used against Vietnam to destroy rice paddies.[5] Agent Blue is a mixture of cacodylic acid (dimethylarsinic acid) and its sodium salt. There was a significant use of coloured arsenic compounds by artists in painting (orpiment, As_2S_3, realgar, As_4S_4) and in wallpaper (Scheele's green, copper arsenite, $CuHAsO_3$ and Schweinfurt (or Schweinfurth) green, also termed Paris green, Vienna green, or emerald green (copper acetoarsenite, $3CuO{\cdot}As_2O_3{\cdot}Cu[OOC{\cdot}CH_3]$).

The concern about the extent of accidental or deliberate poisoning in the 19th century led to the passing of the Sale of Arsenic Regulation Act (1851) which required a signature for the purchase of arsenic compounds.[6] It was largely ineffective and poisoning continued over the next century. Arsenic acid was employed in the manufacture of the second aniline dye, fuchsine or magenta, and this was used to colour foodstuff like sausages or wine, but the dye could still contain enough residual arsenic to prove fatal. Manufacturers persisted in using arsenic acid as the oxidant, which "has led to many lamentable accidents", leading to pleas in 1875 in *Chemical News* to discontinue.[7]

An inspection of the LD_{50} values for a variety of arsenic compounds reveals several interesting aspects. First, arsine, AsH_3, is highly toxic, as are methyl- and dimethyl-arsines, but trimethylarsine is practically non-toxic.[8] Secondly, arsenite is more toxic than arsenate, but methylation reduces the toxicity to practically zero. There are two different mechanisms occurring here: (a) inorganic arsenic poisoning kills by allosteric inhibition of essential metabolic enzymes, leading to death from multi-system organ failure and methylation removes this pathway. And (b) arsine and methylated derivatives, but not trimethylarsine, generate methylarsinyl peroxyl radicals which destroy DNA.[9] There is no doubt that dimethylarsine is highly reactive to air – it spontaneously ignites in air, burning with an orange flame, and generating a white smoke which has surprising sternutatory properties.[10] Another characteristic property of volatile organoarsenic compounds is their intensely unpleasant smell. The odour threshold for trimethylarsine in dilute aqueous solution is found to be 2 ng kg^{-1} leading to the erroneous conclusion that anything so incredibly smelly must be toxic.[11] Which neatly leads us to the question of wallpaper.

In the early 19th century, arsenical green pigments were used to colour wallpaper. It was soon noticed that when mouldy and damp, powerful arsenical odours were generated. This was supposed to be the source of famous poisoning incidents, e.g. Napoleon.[12] The identity of the volatile arsine species was investigated at length by:

Gmelin (1839)	Toxic mould gas
Selmi (1874)	AsH_3
Basedow (1846)	Cacodyl oxide
Gosio (1893)	Alkyl arsine
Biginelli (1893)	Et_2AsH
Klason (1914)	Et_2AsO
Challenger (1933)	Me_3As
McBride & Wolfe	Me_2AsH

Attribution of poisoning due to the evolution of volatile arsenic compounds produced by arsenical compounds in wallpaper is now discredited,[13] but in any case, the amounts generated would be very small, enough to cause ill-health but not death.

The chronic toxicity of inorganic arsenic compounds leading to skin cancers was first noted by Sir Jonathan Hutchinson (1828-1913) in 1887[14] and has been extensively studied.[15] Of current concerns are the chronic health effects of arsenic-contaminated drinking water. The most significant regions affected are in S.E. Asia, in particular West Bengal, and Bangladesh where more than ten million people are at risk. Described by the World Health Organization as "the largest mass poisoning in history", drinking water in these regions commonly contains 0.05-0.2 mg L^{-1} arsenic. A limit of <0.01 mg L^{-1} of arsenic in drinking water is the current WHO recommendation.[16]

Mercury

Mercury was known in ancient times and the metal and its compounds have found diverse uses ever since. In earlier times, it was an essential component of the alchemists' kit and major uses were in silver and gold mining, and in pharmaceutical preparations. More recently, industrial uses such as in the Castner-Kellner cells, in scientific measuring instruments for measuring temperature and pressure and the use in dental amalgams have increased the amount of mercury available in the environment. Other industrial activities, such as coal fired power plants make their contribution too. A natural source of mercury is volcanos. This is dramatically demonstrated from the results of analysis of the ice cores of the Fremont glacier in Wyoming.[17] The pre-industrial level of mercury concentration is about 4 ng L^{-1} then in 1815 there is a spike corresponds to the eruption of a volcano at Tambora in Indonesia, which caused world-wide crop failures. The increase for the years 1850-1875 corresponds to the gold rush and the rise after World War I to the growth in industrial use which declined sharply after about 1985.

While metallic mercury may not be particularly toxic by ingestion, being used in former times as a laxative, probably the only reusable laxative, since it is not readily absorbed, inhalation of the vapour has long been known to cause adverse effects. This was well illustrated during the construction of St Isaac's Cathedral in Saint Petersburg where 100 kg of gold was used to gild a magnificent dome. By the time the construction was complete in 1858, at least sixty workers had died, and possible many more, from mercury poisoning: mercury was used as a solvent for gold.[18] When the Soviets took over, the rich contents of the cathedral were confiscated and the building was converted into the Museum of Atheism, but it is now fully restored.

A selection of LD_{50} values for mercury compounds shows that Hg(I) compounds are usually less toxic than Hg(II), HgS is non-toxic by virtue of its insolubility and dimethyl mercury is by far the most toxic species.

Methyl mercury, CH_3Hg^+, was implicated in the notorious incidents at Minimata Bay in Japan. Nihon Chisso Hiryo–Kabushiki Kaisha (Japan Nitrogenous Fertilizer Company) was set up in 1908 to utilise hydroelectric power to make calcium carbide which was converted into calcium cyanamide and then to calcium nitrate. In addition, the calcium carbide was used as a source of acetylene which was used to manufacture acetaldehyde between 1932 and 1968 using mercury catalysis. Waste water containing CH_3Hg^+ or Hg^{2+} was discharged into the sea where the Hg^{2+} was biomethylated by microorganisms to give CH_3Hg^+ which was bioconcentrated, ending up in fish which was used for human consumption, leading to poisonings and deaths over a period of years.[19,20] Cats were the first to die. They would dance on their hind legs through the streets before plunging into the sea. Cats are enthusiastic fish eaters. Methyl mercury readily crosses the blood-brain barrier, causes ataxia, sensory disturbance and changes in mental state, birth defects and inhibits several stages of neurotransmission in the brain. It is very slowly excreted from the body, unlike inorganic mercury, which has a half-life of about a month. The powerful toxicity of dimethyl mercury was discovered soon after it was first prepared (1852), causing several deaths in 1865.[21]

Potential exposure of the public in Europe to metallic mercury has led to the banning of mercury in glass thermometers (Directive 2007/51/EC), except for scientific purposes, and a recommendation that the emission of mercury from crematoria be cut by 50% by 2012. To achieve this aim, there appears to be two options: (i) fit expensive filters to remove the mercury, which has the on-going expense of collection and disposal of the metal and (ii) close half of the crematoria. There has been a suggestion, from Sweden, that mercury should be captured as HgS which has a very low toxicity due to its insolubility, followed by geological long-term storage.

Lead

Although Pliny noted the toxicity resulting from lead smelting[22]

"While it is being melted, all the apertures in the vessel should be closed, otherwise a noxious vapour is discharged from the furnace, of a deadly nature, to dogs in particular."

and it was generally thought that the use of lead containers to concentrate grape juice created a toxicity hazard, but it is now suggested that chronic lead poisoning did not contribute significantly to the fall of the Roman Empire in the West.[23,24]

But the use of lead containers for food or drink was a source of chronic toxicity for many years. In the 18th century, Devonshire colic was thought to be caused by using lead containers in brewing cider, although this was disputed. Some breweries in the early 19th century advertised their beer as being lead-free. But such a case was reported in the British Medical Journal by a doctor in Morriston, Glamorganshire, in 1900.[25] A man, just referred to as "W.O.", a wheelwright and carpenter in a tin works, became ill:

"At this time [June 1898] there was great prostration and general muscular trembling; he could not stand, he could not lift a cup with his hand, and had scarcely sufficient control of the facial muscles to speak; there was constant vomiting, persistent constipation, pains all over, and progressive loss of flesh."

The cause was unclear for some time. "I then for the first time examined the gums, when at once the explanation of everything became plain, for there was a very decided blue line" – a symptom of lead poisoning. After extensive investigation, the source was revealed. "W.O." on his way to work and on his return, six times a day, was in the habit of taking refreshment at a public house and was always the first customer at 6 a.m. His first pint of the day was beer which had stood overnight in the 20 feet of lead pipe between the cellar and the tap. Analysis showed that this contained lead which proved fatal: "The last I heard of him was that in the following January he fell down in a fit and lingered a few hours before he died.”

Friedrich Christian Accum (1769-1838) drew attention to the use of lead in food, for example, lead chromate to enhance the colour of turmeric, in 1820.[26] But effective legislation was a long time coming. Lead in solder for food and drink tins was only banned in the second half of the 20th century.

In contrast to arsenic and mercury, alkylated lead compounds are not generated in the environment. Ethyl lead compounds were first synthesized by Carl Jacob Löwig (1803-1890) in 1853 by adding iodoethane to a 1:6 alloy of sodium and lead and gently heating.[27] Tetraethyl lead remained a compound of only academic interest for the next 60 years. Thomas Midgley (1889-1944) was an engineer working at the Dayton Research Laboratories, a subsidiary of General Motors, and searching for an anti-knock agent for automobile engines. Years later, he described his success:[28]

> *“[...] we profitably abandoned the Edisonian method in favor of a correlation procedure based on the periodic table. ... Predictions began fulfilling themselves instead of fizzling. Diethyl selenide was prepared and worked as expected; diethyl telluride next fulfilled our predictions. ... The results were plotted as anti-knock effect vs. atomic number. Tin was the first element investigated from the group immediately to the left of those previously reported. Its ethyl derivative was studied. This compound exhibited a much more powerful effect than had been expected. We thereupon predicted that tetraethyl lead would solve the problem.”*

The results he obtained are illustrated in **Figure 1**.[29]

Midgley promoted tetraethyllead (TEL) as a superior anti-knock agent to ethanol, and it was more profitable too. Production commenced in 1923 but was soon temporarily halted when production workers became ill (hallucinations, madness) and died. Midgley needed a holiday in Florida to recover from the effects after demonstrating the safety of TEL. Following improvements in the handling, and studies funded by the Ethyl Corporation, which proved that TEL was safe, production resumed. Posters announced ‘Ethyl is back’. It stayed until Congress finally outlawed it completely (in the US) in 1989. Later in life, Midgley introduced the world to chlorofluorocarbon refrigerant gases.[30]

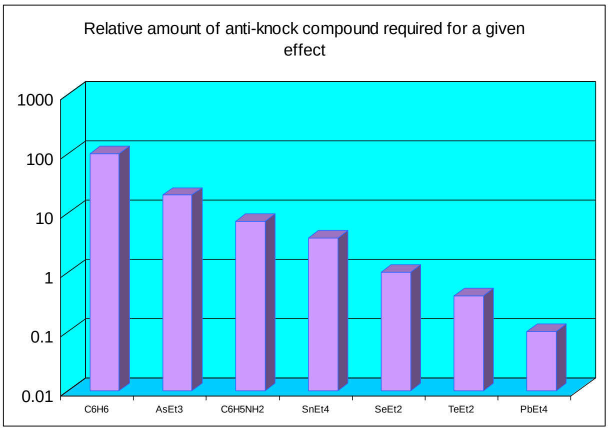


Figure 1: *Comparison of anti-knock compounds.* ***Far left:*** *benzene;* ***far right:*** *tetraethyllead*

The year before TEL was unleashed on the world, Clair Cameron Patterson (1922-1995) was born, an Iowa farm boy, in spite of his first name. Researching at the University of Chicago, he elected to work on determining the uranium/lead isotopic ratios, using mass spectrometry, in old minerals with a view to estimating the age of the Earth. He concluded, in 1953, that the answer was 4550 million years, a figure that still stands today. His big problem was to find minerals which were not contaminated with modern lead and then to do measurements in an uncontaminated environment. The source of the contamination, he decided, was from lead in petrol and he campaigned for many years for its removal, attracting the wrath of the big oil companies.[31] He was eventually successful.[32] This is illustrated in **Figure 2** by the amount of lead used in gasoline additives over a 30-year period.[33]

Production of TEL ceased in the US and Canada and was moved to Ellesmere Port in Cheshire, where it continued for a few years until, following fires and explosions, it was moved elsewhere. Following the removal of lead in petrol in the US, a 90% reduction in the mean blood lead level concentration occurred between 1976 and 1995.

Cadmium

In contrast to arsenic, mercury and lead, cadmium is a recent discovery (1817). The discoverers were either Karl Samuel Leberecht Hermann (1765-1846) or Friedrich Stromeyer (1776-1835). It is usually associated with zinc. Cadmium was widely used in plating to protect other metals from corrosion and as a pigment (CdS, CdSe). The toxicity of cadmium compounds was first reported in 1858 when it was found that exposure to cadmium carbonate dust used in silver polishing caused respiratory and gastrointestinal symptoms.[34] The first chronic poisoning, causing rhinitis and pharyngitis in plating workers, was reported in 1940.[35] By the 1950s the hazards of working with cadmium were well

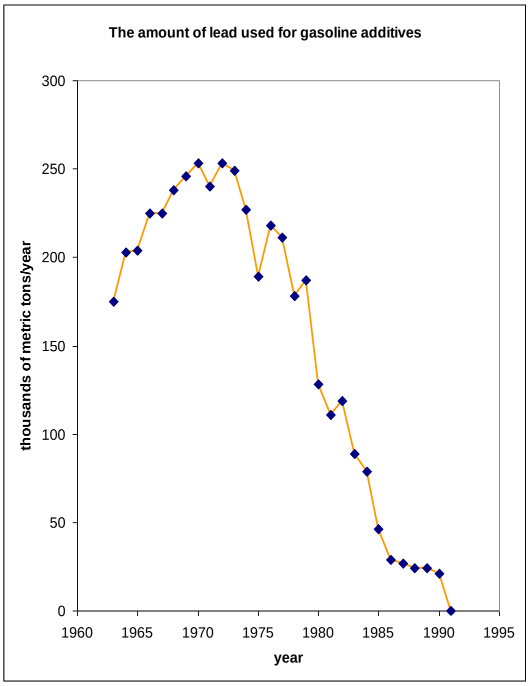


Figure 2: *Decline in the use of lead in gasoline additives.*

established, causing emphysema and proteinuria from inhalation.[36]

Chronic poisoning by cadmium has been reported at several locations worldwide.[37] The symptoms are renal osteomalacia caused by a build-up of cadmium in the kidneys leading to a bone disease with fractures and severe pain.[38] The most notorious case occurred in Japan where the disease is known as *itai-itai* (Ouch! Ouch!). In 1910, the Mitsui Mining & Smelting Co Ltd started operations at the Kamioka Mines in the Toyama Prefecture where lead, copper and zinc were the major products. Waste water was discharged into the Jinzu River. The first poisoning was reported in 1912. Between 1939 and 1954, 200 people were affected by *itai-itai* and 100 died, but the cause of the illness was unknown at that time. In a December 1957 medical symposium in the Toyama Prefecture, a participating doctor, Dr. Noboru Hagino, suggested in a paper that *itai-itai* disease was caused by waste water from the factories. By 1961, he had narrowed down the source to cadmium discharged during mining activities in Kamioka by the Mitsui Mining Company.[39] The evidence was convincing. Comparing the incidence (prevalence) of *itai-itai* with the level of cadmium pollution showed a high correlation.[40]

The World Health Organization in its International Program on Chemical Safety, WHO/IPCS, reports that a drinking-water guideline value of 0.005 mg/litre for cadmium was set in 1984.[41]

Conclusion

The health concerns of heavy metals and metalloids have been evident for a long time, but were often disregarded when commercial gain took precedence.

References

1. Trevan, J. W. The error of determination of toxicity. *Proceedings of the Royal Society of London*, 1927, **101B**, 483-514.
2. Hodge, H. C. and Sterner, J. H. Tabulation of toxicity classes. *American Industrial Hygiene Association Quarterly*, 1949, **10**(4), 93-96.
3. CLP-Regulation (EC) No 1272/2008.
4. McCann, M. Arsenic and other preservatives in museum specimens. *Art Hazards News*, 1995, **18**(2), 1-2.
5. Stellman, J. M., Stellman, S. D., Christian, R., Weber, T. and Tomasallo, C. The Extent and patterns of usage of Agent Orange and other herbicides in Vietnam. *Nature*, 2003, **422**, 681-687.
6. Bartrip, P. A. "Pennurth of Arsenic for Rat Poison": The Arsenic Act, 1851 and the prevention of secret poisoning. *Medical History*, 1992, **36**, 53-69.
7. Anon. The production of aniline colours without the use of arsenic acid. *Chemical News*, 1875, **31**, 40.
8. Yamauchi, H., Kaise, T., Takahashi, K. and Yamamura, Y. Toxicity and metabolism of trimethylarsine in mice and hamsters. *Fundamental Applied Toxicology*, 1990, **14**, 399-407.
9. Yamanaka, K., Hoshino, M., Okamoto, M., Sawamura, R., Hasegawa, A. and Okada S. Induction of DNA damage by dimethylarsine, a metabolite of inorganic arsenics, is for the major part likely due to its peroxyl radical. *Biochemical and Biophysics Research Communications*, 1990, **168**(1), 58-64.
10. The author, personal observation.
11. Cullen, W. R. and Reimer, K. J. Arsenic speciation in the environment. *Chemical Reviews*, 1989, **89**, 713-764.
12. Jones, D. E. H. and Ledingham, K. W. D. Arsenic in Napoleon's wallpaper. *Nature*, 1982, **299**, 626-627.
13. Cullen, W. R. and Bentley, R. The toxicity of trimethylarsine: an urban myth. *Journal of Environmental Monitoring*, 2005, **7**, 11-15.
14. Hutchinson, J. Arsenic cancer. *British Medical Journal*, 1887, **2**, 1280.
15. Neubauer, O. Arsenical cancer: A review. *British Journal of Cancer*. 1947, **1**(2), 192-251.
16. *Environmental Health Criteria 224 : ARSENIC AND ARSENIC COMPOUNDS*, 2nd edn., pp 501, World Health Organization, Geneva, 2001.
17. Schuster, P. F., Krabbenhoft, D. P., Naftz, D. L., Cecil, L. D., Olson, M. L., Dewild, J. F., Susong, D. D., Green, J. R. and Abbott, M. L. Atmospheric mercury deposition during the last 270 Years: A glacial ice core

record of natural and anthropogenic sources. *Environmental Science and Technology*, 2002, **36**(11), 2303-2310.
18. http://www.nevsky-prospekt.com/isaacs.html (accessed 25 November 2011).
19. Thayer, J. S. Biological methylation – its nature and scope, *Journal of Chemical Education*, 1973, **50**(6), 390-391.
20. Jensen, S. and Jernelöv, A. Biological methylation of mercury in aquatic organisms. *Nature*, 1969, **223**, 753; doi:10.1038/223753a0.
21. Edwards, G. N. Two cases of poisoning by mercuric methide. *St Bartholomew's Hospital Reports, Vol. 1*, Longmans, Green, and Co., London, 1865, pp 141-150.
22. Pliny the Elder. *Historia Naturalis*, xxxiv, **50**, 167.
23. Retief, F. P. and Cilliers L. Lead poisoning in Ancient Rome. *Acta Theologica*, 2006, **26**(2), 147-164.
24. Scarborough, J. The myth of lead poisoning among Romans: an essay reviewed, *Journal of the History of Medicine*, 1984, **39**, 469-75.
25. Morgan, E. R. A case of lead poisoning by beer. *British Medical Journal*, 1900, 1373.
26. Accum, F. C. *A treatise on adulterations of food and culinary poisons, exhibiting the fraudulent sophistications of bread, beer, wine, spirituous liquors, tea, coffee, cream, confectionary, vinegar, mustard, pepper, cheese, olive oil, pickles, and other articles employed in domestic economy, and methods of detecting them*. Milner and Company, London, 1820.
27. Löwig, C. J. Ueber Methplumbäthyl. *Annalen der Chemie*, 1853, **88**, 318-323; *Journal für Praktische Chemie*, 1853, **60**, 304-310.
28. Nickerson, S. P. Tetraethyl Lead: A product of American research. *Journal of Chemical Education*, 1954, **31**, 569.
29. Replotted on a logarithmic scale from data in reference 28.
30. "Leaded Gasoline, Safe Refrigeration, and Thomas Midgley, Jr." Chapter 6 in McGrayne, S. B., *Prometheans in the Lab: Chemistry and the Making of the Modern World*, McGraw-Hill, New York, 2002; ISBN 0-07-140795-2.
31. Patterson, C. C. Contaminated and natural lead environments of man. *Archives of Environmental Health*, 1965, **11**, 344-360.
32. Bryson, B. "Getting the lead out" in *A Short History of Nearly Everything*, Black Swan, London 2004, pp 193-205.
33. Data from http://minerals.usgs.gov/minerals/pubs/commodity/lead/stat/tbl2.txt; 1987-91 U.S. Department of Commerce estimate.
34. Sovet, A. Poisoning caused by powder used in cleaning of silver. *Presse Med. Belge.*, 1858, **10**, 69-70.
35. Mancioli, G. Le alterazioni rinofaringee nei lavoratori del cadmio. *Rassegna di medicina industriale e di igiene del lavoro*, 1940, **11**, 632.
36. Bonnell, J. A. Emphysema and proteinuria in men casting copper-cadmium alloys. *British Journal of Industrial Medicine*, 1955, **12**, 181.
37. Kjellstrom, T. Exposure and accumulation of cadmium in populations from Japan, the United States, and Sweden. *Environmental Health Perspectives*, 1979, **28**, 169-197.
38. Nordberg, G. F. New insights into the mechanisms of cadmium toxicity: Advances in cadmium research. *Toxicology and Applied Pharmacology*, 2009, **238**(3), 192-200.
39. Makoto, K. Research history of Itai-Itai disease for 56 years and future problems in the 21st Century. *Itaii-taibyo Shori Hanketsu 30shunen Shinpojiumu*, 2003, 5-20. (Japanese; English abstract) http://sciencelinks.jp/j-east/article/200311/000020031103A0341096.php
40. http://www1.wlsh.tyc.edu.tw/~globalschoolnet/a6.html (accessed 4 December 2011)
41. *Cadmium. Environmental Health Criteria Document 134*, IPCS. WHO, Geneva, 1992, pp 1-280.

CHRIS COOKSEY

dha@chriscooksey.demon.co.uk

*The golden domes of **St Isaac's cathedral in Saint Petersburg.** At least 60 workman died from inhaling mercury fumes during the gilding processes for the domes.*

This article is based on a presentation by Chris Cooksey at the joint ECG/Historical Group Symposium 'Environmental Chemistry: A Historical Perspective' *held at Burlington House on 26th October 2011.*

Meeting report

Toxicology of metallic nanoparticles

On 24th June 2011, the RSC Toxicology group held a one-day meeting on the ‘Role of metals in the toxicity of nanoparticles: Informing the regulation of nanoparticulate safety’. The aim was to give an overview of the recent research in this area and to collate the toxicological opinions, particularly with reference to regulation. The current concern over the potential toxicity of nanoparticles (environmental, clinical and engineered) is often based on presumptions and uncertainties in their various modes of action. Greater understanding of the specific mechanisms would aid the risk assessment process.

Dr Andy Smith (MRC, Leicester) introduced the meeting giving his view of the current lack of knowledge of toxicological mechanisms for metallic nanoparticles (NPs) and the tendency to presumption of the mode of action by grouping certain species. He posed a number of questions for the day including:

- How might metallic nanoparticles contribute to toxic and carcinogenic processes?
- Does the nano state have a specific role to play, other than as a provider of metallic ions?

Professor Ken Donaldson (University of Edinburgh) then covered a number of studies that had looked at various aspects of metallic nanoparticulate toxicology and presented data that he had compiled from a number of sources. First, he presented a number of data that demonstrated that smaller particles were better translocated (e.g. gold where a 10-fold increase in translocation across the lung air/blood barrier was seen for a 10-fold reduction in particle size) and caused greater inflammation. The inflammation was related to surface area in a linear response, across a number of particle types. He then went on to discuss the role of surface chemistry – different metal oxide NPs with the same surface area showed markedly different free radical activity. For insoluble particles, positive acid zeta potential seems to increase inflammation responses. For soluble particles, the toxicological impact seems directly related to the toxicity of the soluble species, for example Cu^{2+} and Zn^{2+} ions (from metal NPs) are highly toxic and inflammogenic whereas Mg^{2+} ions are not. Professor Donaldson finished his presentation with a discussion of metallic nanofibres and whether they fit the ‘asbestos paradigm’, where the toxicity is related to the high aspect ratio (AR) of the fibre. Metallic nanofibres can exist as nanorods (AR up to 5) and nanowires (AR up to 1000). Inflammation tests have shown that there is very little response to fibres less than 5 µm in length; beyond this ‘trigger point’ there is a dramatic increase in inflammation, with an apparent length related increase up to ~20 µm after which the response plateaus.

Professor Terry Tetley (Imperial College, London) followed with a presentation on the reactivity of NPs in the lung, specifically at the alveolar interface. It is estimated that 50% of inhaled nano-sized objects will reach the alveoli. The alveolar surface consists of two cell types, type one (AT1) epithelial cells which cover 95% of the alveolar surface and type 2 (AT2) which are progenitors to AT1 cells. Professor Tetley’s research group has undertaken a range of *in vitro* experiments, looking for AT1 cell responses to NP challenge. Little difference in IL-8 response was seen on dosing with TiO_2, Ag, tungsten carbide (WC) or ZnO NPs. However, IL-6 response was increased for all NPs and all doses with responses still elevated after 48 hours recovery (except for ZnO) although Ag and ZnO caused cell death at the higher doses. Polydispersed 244 nm Ag particles caused a significant increase in IL-8 whereas other smaller Ag particles (5 – 44 nm) with various coatings (sugar, PVP, citrate) didn’t alter IL-8 release. The use of foetal calf serum (FCS, widely used in tissue culture) can also influence cell death and IL-6/IL-8 release – for CuO NPs the TD_{50} was reduced 3 -fold in the presence of FCS compared to without, whereas for ZnO the TD_{50} was doubled in the presence of FCS (TiO2 was unaffected). Experiments looking at the effect of different forms of TiO_2 on AT1 cell mediator releases showed that nanopowder (~600 nm) was no more likely to result in IL-6, IL-8 or MCP-1 release than standard TiO_2 (~950 nm), pure anatase (~300 nm) or pure rutile (~150 nm).

Next, **Professor Jamie Lead** (University of Birmingham) gave an overview of research into silver nanoparticles in the environment. In the environment NPs acquire coatings of organic matter (humus), this can cause aggregates of around 2.5 µm to disaggregate into ~30 nm particles over a 30-day period. Silver NPs were shown to be highly toxic to *Pseudomonas sp.* when incubated in media alone but there was no observed effect on growth when incubated in humus-containing media. By contrast humus had no effect on the high toxicity of silver nitrate. The media causes aggregation so the high toxic response of silver NPs is therefore not explained by dissolution.

Professor Frank Kelly (King’s College, London) presented results from a study on ambient particulate matter (PM) toxicity. It has been estimated that 29,000 deaths are due to airborne particles. In cities, most of the particulate matter comes from traffic pollution and the problem has been exacerbated by the increase in the use of diesel. Particles consist of a carbonaceous core with components adsorbed onto the surface (organics e.g. PAHs, metals, biological material e.g. endotoxins). Three sites (semi-rural, urban residential and high urban traffic) were studied for oxidative potential of the PM collected at each site – the high urban traffic area showed greater oxidative potential (both as a fraction of PM and per unit volume air) than the other sites. The RAPTES (Risk of Airborne Particulates: A hybrid Toxicological-Epidemiological Study) study aims to assess the metal content and redox activity of ambient PM during human volunteer challenge. Volunteers were exposed to an underground train platform environment as well as a traffic intersection and an urban garden. Ambient iron-containing PM concentrations were 100 times greater and $PM_{0.18}$ concentrations were 300 times greater in the underground scenario. Nasal lavage samples showed that post-underground levels of iron PM deposits were three times greater than for the other scenarios. There was also evidence of increased redox activity of the PM deposited in the nasal cavity and this activity was correlated to the iron content of the nasal lavage fluid.

Continuing the iron theme, **Dr Shareen Doak** (University of Swansea) is studying the genotoxicity of iron oxide NPs. Ultrafine superparamagnetic iron oxide nanoparticles (USPION) have potential medical applications in MRI imaging, drug delivery and magnetic tumour ablation. There are three different composition types – Fe_3O_4, γ-Fe_2O_3 and α-Fe_2O_3 and the supramagnetic properties rely on a particle size of <35 nm. *In vitro* experiments showed that serum content had an impact on apparent hydrodynamic diameter (at 1% serum average diameter was nine times greater than at 10% serum for the same nominal 10 nm particles). Cellular uptake of dextran-coated Fe_2O_3 was three times greater in 1% serum than 10% and also three times greater than dextran-coated Fe_3O_4. However, uncoated Fe_2O_3 was absorbed to the same extent as uncoated Fe_3O_4 and the amount of serum did not affect uptake. Fe_2O_3 particles were shown to cause dose-dependent increased oxidative NA adducts and the cellular response was similar to iron overload in hepatocytes.

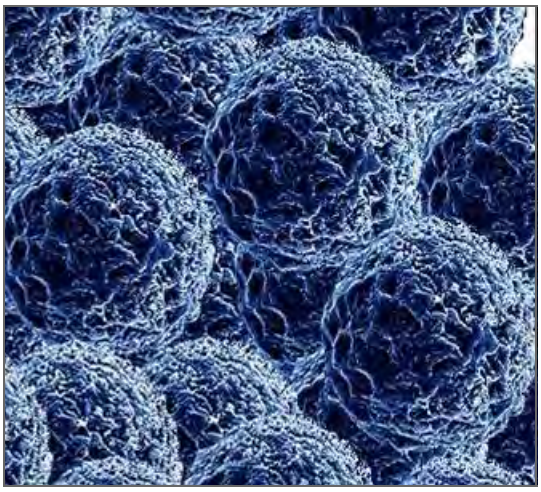
Dr Patrick Case (University of Bristol) concluded the day's presentations with a study on cobalt and chromium NPs *in vitro* and *in vivo*. Metal-on-metal (MoM) replacement joints are becoming increasingly common as younger patients receive implants. Although MoM implants have been used since the 1930s, two new adverse reactions have been observed. Within five years of surgery, 1% of patients suffer 'pseudotumours' destroying local tissues, or local 'hypersensitivity' immune reactions. Long-term risks include melanoma (up 43%), kidney (up 22%) and bladder (up 15%) cancers after 10 years. *In vitro*, CoCr NPs were more cytotoxic and caused more DNA damage than an equivalent micron-sized particle dose. *In vivo*, blood and urine levels of Co or Cr are increased post-operation from six months to at least 2 years. Chromosomal aberrations also increase. In 2010 a medical device alert was issued describing the potential adverse immune reactions. In cases where replacement surgery is required, corrosion of the implant has been observed.

Following the presentations there was a brief discussion of the issues. The general consensus was that nanoparticle toxicology seemed to be very complicated! There seemed no apparent clear case for groupings, although "low toxicity" NPs might be filtered out on surface area/inflammation ratios. It is also perhaps reasonable that nanofibres are considered on their physical properties, such as aspect ratio. It is clear that NPs are not a single entity and surface reactivity may be important in determining toxicology. Routes of entry also seem to be relevant and *in vitro* experiments may not always reflect what is seen *in vivo*.

KATE JONES
Principal Scientist,
Health & Safety Laboratory, UK

Reproduced with permission from the RSC *Toxicology Group Newsletter*, Autumn/Winter 2011.

Visit the Toxicology Group web pages at http://www.rsc.org/Membership/Networking/InterestGroups/Toxicology/Meetings.asp for the PowerPoint presentations from this meeting.



Forthcoming Symposium

Royal Society of Chemistry Historical Group

“Where there’s muck there’s brass”. The Reclamation of Chemical Sites

A one-day meeting at the Chemistry Centre, Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN on Friday, March 23rd, 2012

PROGRAMME

10.30	**Coffee and tea**
11.00	**Welcome** (Prof. Bill Griffith, Secretary of Historical Group)
11.05	**Introduction to Themes of the Meeting** Dr David Leaback/Peter Reed
11.15	**The Remediation of the Olympic Park – The First Gold Medal.** Martyn Lass and James Apted (Atkins)
12.00	**The Remediation of Three London Dye-works Sites Known to me** Dr David Leaback
12.45	**LUNCH** This is not provided but there are many cafés, sandwich bars and pubs nearby.
14.00	**“Galligu” and the Alkali Industry in Lancashire, Tyneside and Glasgow** Peter Reed
14.45	**Cu @ Swansea: The Reclamation and Regeneration of the Lower Swansea Valley.** Professor Huw Bowen (Swansea University)
15.30	**TEA**
15.45	**Brownfield Site or Industrial Heritage? Assessing the Historic Value of Former Explosives Sites.** Wayne Cocroft (English Heritage).
16.30	**Sites with Radioactivity** Shaun Amos (AWE, Aldermaston)
17.15	**Concluding Remarks** Professor Jack Betteridge
17.30	**Close of Meeting**

REGISTRATION FORM

Advance registration and pre-payment is essential. I wish to attend the RSCHG Meeting “*Where there’s Muck there’s Brass”. The Reclamation of Chemical Sites* and I enclose a cheque for **£10**, payable to the RSC Historical Group. This charge includes morning and afternoon tea or coffee.

Name……………………………………….. e-mail address………………………………….....................

Address (please print)……………………………………………………………………………….............

......…………………………………………………………………. (Postcode)……………………… ...

To register, please e-mail Bill Griffith (w.griffith@ic.ac.uk) **and send a cheque for £10, using the form above**, payable to '**RSC Historical Group**' to **Dr. John Hudson, Graythwaite, Loweswater, Cockermouth, Cumbria CA13 0SU.** Receipt of cheques will be acknowledged to applicants who give their e-mail address. For any problems or queries please contact Bill Griffith at w.griffith@ic.ac.uk.

Book review

Carbofuran and Wildlife Poisoning: Global Perspectives and Forensic Approaches

Ngaio Richards (Editor)

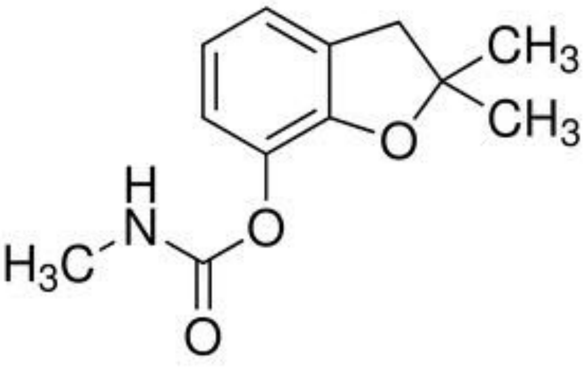
Wiley Blackwell, Chichester, UK,
November 2011, pp xxvi + 277,
ISBN 978-0-470-74523-6, £90.00
(hardcover)

Carbofuran and Wildlife Poisoning: Global Perspectives and Forensic Approaches describes the legal and illegal uses of the pesticide Carbofuran and its environmental effects in a number of countries throughout the world. Each chapter has scientific depth with the overall style almost as a narrative of the discovery of the problems arising from the use of Carbofuran. The book is multidisciplinary throughout, indeed emphasising that such an approach is necessary to control the risks posed by this product. Each chapter is written by locally-based experts in the field and is well cross-referenced. Simple introductions to each of the chapters are helpful when delving into less familiar topics and make the text very readable. The book as a whole is well referenced to January 2011.

Carbofuran is a systemic carbamate insecticide and is also used as an acaricide and a nematocide.

The acute toxicity of Carbofuran has been evaluated in several species. The reported oral LD_{50}s are 6.4 to 14.1 mg/kg for rats, 18.5 mg/kg for dogs, and 25 to 38.9 mg/kg for chickens. Mice appear to be less sensitive to the toxicity of Carbofuran as the median lethal doses ranged from 250 to 500 mg/kg. The lethal effects of Carbofuran are due largely to the chemical's direct inhibition of acetylcholinesterase. Ultimate cause of death is respiratory failure. Signs and symptoms of cholinesterase poisoning occur within minutes as Carbofuran acts directly on the enzyme without metabolic activation. Variations in species sensitivity probably reflect species differences in metabolic deactivation of Carbofuran to its less potent metabolic products. The compound is sparingly soluble in water (700 mg L^{-1}) and has the potential to contaminate aquatic resources. Exposure of wildlife can be through direct ingestion or *via* contaminated water¸ soil and sediments. Illegal baiting should also be included. Degradation is very environment specific but it tends to be more stable in acidic soils. Photochemical degradation, occurring particularly in tropical and subtropical regions, can produce products which are more toxic than the original compound.

The broad effect range of Carbofuran has led to its worldwide use including control on sugar cane, sugar beet, maize, coffee and rice crops. It is sold in a number of formulations including liquid, silica-based and granular forms. Carbofuran has been commercially available since 1967 and although it can be seen as old-fashioned compared with later pesticides, which discriminate between target and non-target organisms, it still has a market in territories where it is not prohibited. Introductory chapters give an overview of the problem and the impact on birds. Birds are particularly susceptible to poisoning though the scientific reason behind this is unclear. The median LD_{50} for a range of birds is 1.65 mg/kg.



Carbofuran: 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate

The editor's original research was on the decline in population of vultures in Kenya, and she quickly discovered the major contribution of Carbofuran in this decline. In other parts of the world Carbofuran may also be a significant contributing factor to the loss of wildlife. The choice of the formulation may be part of the problem, birds often seeing granular formulations as seed. It is almost totally lacking in odour and taste. The chapters describe the different ways wildlife can be exposed, signs that can be used to recognise intoxication, diagnosis of Carbofuran kills and how poisoned birds can be rehabilitated.

Following a chapter of the concerns in Kenya, the book discusses the problem in other parts of the developing and developed world, the few areas not covered being summarised in an Appendix. Different emphases are found between the geographical areas. Reports from the developed world emphasise legislation and scientific studies of potential impact.

Less developed areas concentrate more on sustainability and tackling illegal use, and these topics are discussed in terms of a human – wildlife conflict. In Kenya, the main problems of illegal bush-meat and 'pest' control directly affect such species as crocodiles, squirrels and hawks. Anecdotal evidence suggests that poisoning of lions may be attributable to Carbofuran, other poisons being less readily available. These species are already threatened environmentally and are also a major source of revenue through tourism. Though attempts have been made to restrict its availability, Carbofuran may still be obtained in Kenya. The problems from the human – wildlife conflict are developed further in the chapter on India though, in this region, Carbofuran is not the pesticide of choice for illegal killings. The chapter covering Latin America discusses mitigating the effect of legal usage with repellents, colouration and camouflaging. The lack of methods of safe use for wildlife is reflected in the detailed analysis of the impact of formulations in the US.

Restrictions or cancelled registration for the use of Carbofuran products are now in place in all the developed territories studied (EU, US, Canada), but Carbofuran-related wildlife mortality continues. So little pesticide is needed for illegal bird-kills that the problem may well continue for many years even with remaining stocks of the pesticide, and one cited reference, referring to Scotland, showed that Carbofuran was the most used pesticide for illegal activities.

Carbofuran and Wildlife Poisoning: Global Perspectives and Forensic Approaches is useful for anyone who wishes to gain insight into the complexities of current global environmental problems and control as well as those interested in the narrower area of Carbofuran use and abuse.

Reviewed by **Dr ROGER REEVE**

University of Sunderland

Africa has lost 180,000 of her lions in the past 30 years alone due to habitat loss, hunting and killing, and indirectly by the misuse of substances such as Carbofuran. That is a decline of 90% of the lion population. WildlifeDirect, started by the palaeontologist and conservationist Richard Leakey, is helping conservationists on the ground to save this endangered species. http://wildlifedirect.org/

Forthcoming Symposium

RSC Environmental Chemistry Group & RSC Environment, Sustainability & Energy Division

2012 ECG Distinguished Guest Lecture & Symposium

Energy, Waste & Resources – three sides of the same coin?

A one-day symposium organised by the RSC Environmental Chemistry Group and the Environment, Sustainability and Energy Division of the Royal Society of Chemistry, incorporating the **2012 ECG Distinguished Guest Lecture** to be given by **Prof. Paul Williams** (University of Leeds).

The Royal Society of Chemistry, Burlington House, Piccadilly, London, Wednesday 14th March 2012

Programme

1200 **Registration;** Lunch & Coffee

1300 **Mr James Cooper, Head of Energy-from-Waste Policy, DEFRA**

Energy from Waste: A policy perspective

Mr David Brignall, Wardell Armstrong

Pyrolysis and gasification – planning and environmental impacts

Mr Kris Wadrop, Solvert Ltd

Where there's muck there's n-butanol! (and a range of other high value chemicals)

1430 Tea/Coffee; **ECG Annual General Meeting**

1500 **Dr Raffaella Villa, Cranfield University**

Organic waste disposal: emissions and risks

DGL: Prof Paul Williams, University of Leeds

Fuels, chemicals and materials from waste

General Discussion

1715 Close

To register online, or download a hard copy registration form, please see **www.rsc.org/ecg** and choose “Forthcoming Events”. For further details please contact w.j.bloss@bham.ac.uk

Admission is by ticket only. In order to register for this meeting, please **register online** *via* www.rsc.org/ecg, or complete the form on p 35 and return by post (see details below).

There is a charge of £25 for members of the ECG and £50 for non-members of the ECG (£25 concessions, i.e. student/unwaged; proof required). Cheques should be returned with this form (made payable to *RSC Environmental Chemistry Group*). **Early application is encouraged as places are limited and will be allocated on a first come first served basis.**

A limited number of places are reserved free for retired members; these will also be allocated on a first come first served basis. We are able to offer limited travel bursaries for current students – please email Dr Bloss if you would like to be considered for one of these.

Name ……………………………………………………………………………….........

Affiliation ………………………………………………………………………………..

Address …………………………………………………………………………..........

………………………………………………………………………………...................

………………………………………………………………………………...................

Email address ………………………………………………………………………..

I would like to attend: ☐ **Energy, Waste & Resources symposium** ☐ **The ECG AGM**

I enclose a cheque for:

☐ **£50 (non-member)**

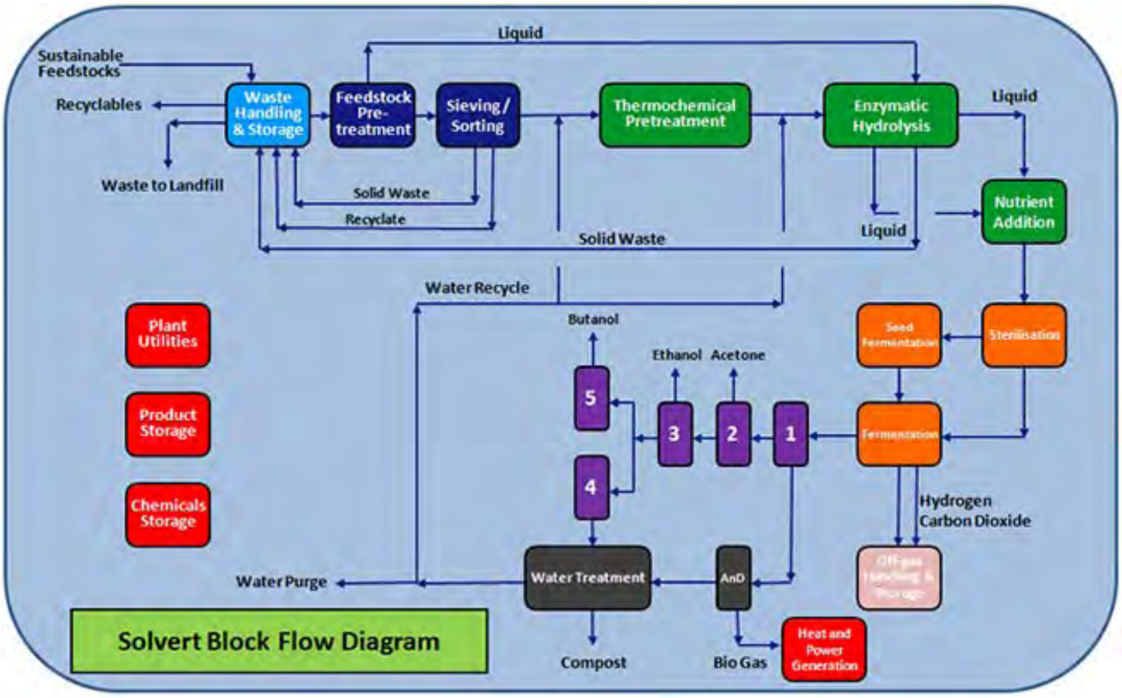
☐ **£25 (ECG members/non-ECG concessions) RSC membership no: ……..**

☐ **I would like to attend as a retired RSC and ECG member**

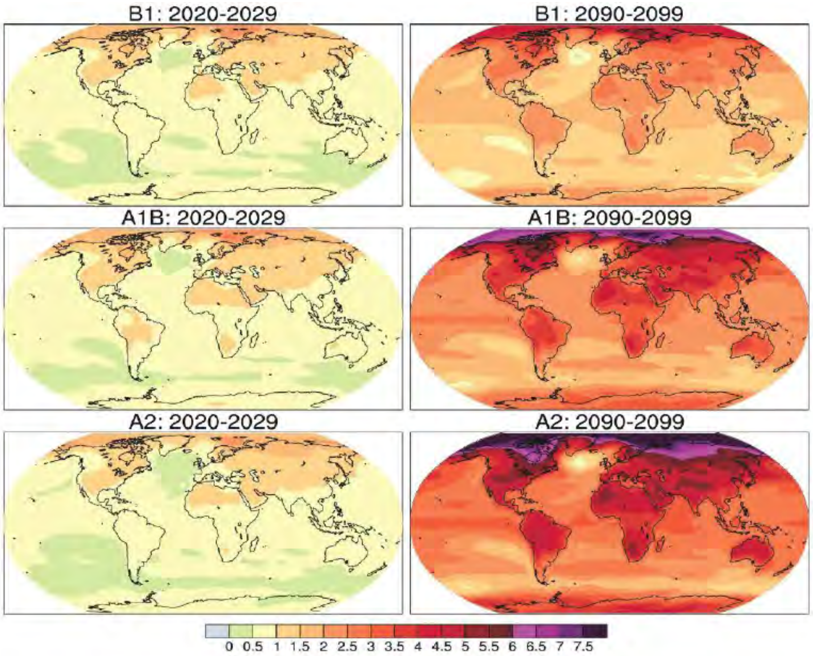
Dietary/access requirements: ……………………………………………………...

Signed .... **Date** ....

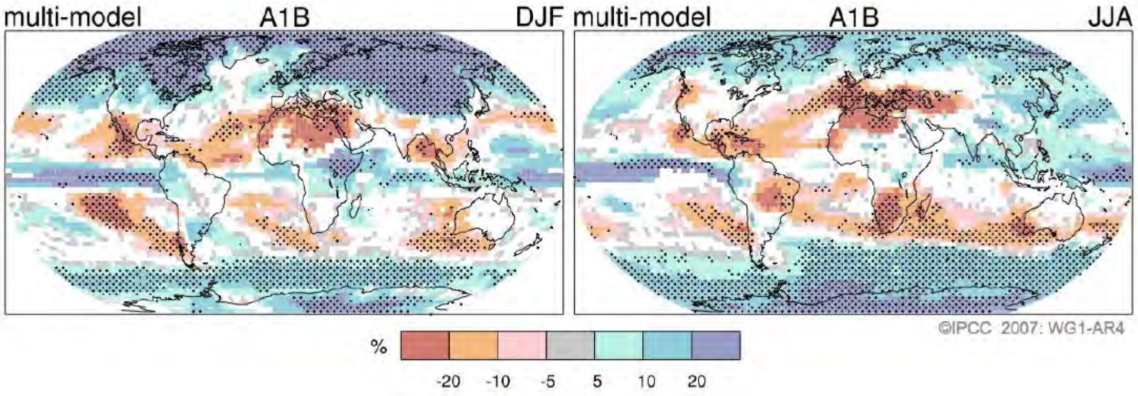
Please return to: Dr William Bloss, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT Tel. 0121 414 255 Fax 0121 414 3709
Email w.j.bloss@bham.ac.uk



Projected warming in 21st century expected to be greatest over land and at most high northern latitudes and least over the Southern Ocean and parts of the North Atlantic Ocean



Projected Patterns of Precipitation Changes



Precipitation increases *very likely* in high latitudes

Decreases *likely* in most subtropical land regions

Two future climate scenarios for the 21st century

(From Professor Simon Tett's presentation at the joint ECG/Historical Group Symposium 'Environmental Chemistry: A Historical Perspective' *held at Burlington House on 26th October 2011. See pp 9-11).*

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 Regal Print & T-Shirt Co Ltd, Unit 5, Dinnages Business Park, 22 Wivelsfield Road, Haywards Heath, West Sussex RH16 4EQ. Tel.: 01444 456673