January 2012

Royal Society of Chemistry
Environmental Chemistry Group

ISSN 1758-6224 (Print) 2040-1469 (Online)
www.rsc.org/ecg

Bulletin

Tyndall Glacier, Rocky National Park, Colorado

"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, S 7\QGDOO¶V LQWHUHVW LQ 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 àº,U3ÖÚx¨SÇ9ÝbzT¿ž•lµÊV ’ôYY²ÃÇ¶ÅW§#ž= öó Äë¦9Œ0v™óà³W BžîÑŸ…Œj”S CÉ[>12F editions of the ECG Bulletin . A report of a recent meeting on the toxicology of metallic nanoparticles organised by the 56&¶V 7R[LFRORJ\ *URXS $QG details of the 2012 ECG Distinguished Guest Lecture and accompanying symposium at Burlington House, London in March.

Also

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ECG Symposia: ‘The Nitrogen Cycle’ was the topic for the

, held at Burlingby contacting the membership department at membership@rsc.org

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 anthro4

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 (Emeritus Professor at the University of Leeds) opened and chaired the proceedings.

The opening speaker was from the University of Edinburgh who spoke on “Anthropogenic CO_2 and climate change –an frotlẌ2 friended 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 18568n p1i96(w15(a)4(s)-(l)-99(th)-6(a)4(t)-96(se)4(v)7(e)4a(e)4(l)-14( )]TJ 0 -11.88 TD 4(g)7(e)o(u)-6(g)r3(a)

The final talk was given by 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, , 483) and its subsequent translation into simple scales. [(Hodge and Sterner Scale –

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

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.*, , 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.*, , 165-173.

G. S. Callendar (1938). The artificial production of carbon dioxide. *Q. J. R. Meteorol. Soc.*, , 223-240. (Available

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, pth andta66( )-297( )-2(a8)-54(c)a6(v)7(e)4(d)-6( )-29(b)5(h)-6(e)4(n84( )-169(h)-6)-213(m)18(o)-6(vr-6(v)7(e)4(d966( )-2it)-14(y93( )-13i 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 ( ). 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.

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 O[RfnMr––nJF;ŸRIWKHPHFKDQ and taking the appropriate so46>4ial, economic and poliRlJAL@&fqHägnAvjAŽavñFSEO[YfqvPĜHg(bnB6ŽĉÑ

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Further reading

1. A. S. Eve and C. H. Creasey, *Life and Work of John Tyndall*, Macmillan & Co., London, 1945.

2. N. D. M526mcM526millan, R. C. M59mollan and W. H. Brock (editors), *John Tyndall: Essays on a NatuB18<ral Phil9moso-pher*
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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

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,

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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 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*, , 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.

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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.

After a rather unpromising start (he obtained a third class London external degree in Chemistry from Derby Technical

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 R€

Further reading

1. ‘Frederick Challenger 1887-1983: chemist and biochemist’, T. G. Chasteen and R. Bentley, *Appl. Organomet. Chem.*, 2003, , 201.

2.

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 tr21(y)20(late)4(d)11.88 TD [(d)-614(w) /P <</MCID7-atedT*[(m)5(]TJ 0 -11,5)-6(i)-8(m)178noer7ylated

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,

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, , 483-514.
2. Hodge, H. C. and Sterner, J. H. Tabulation of toxicity classes. *American Industrial Hygiene Association Quarterly*, 1949, (4), 93-96.
3. , 1-941Bd2( )]TJ72.36T5 9 Tf 0 Tc 27 0 T2(rte)4(rly)]JTf 19 [(()13(4

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.

(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?

(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 εm in length; beyond this ‘trigger point’ there is a dramatic increase in inflammation, with an apparent length related increase up to ~20 εm after which the response plateaus.

(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 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. Vne

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Two future climate scenarios for the 21st century

(From Professor Simon Tett’s presentation at the joint ECG/Historical Group Symposium ‘Environmental Chemistry: A History recalled’ 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