Royal Society of Chemistry

ISSN 1758-6224 (Print) 2040-1469 (Online)

Environmental Chemistry Group

Bulletin



www.rsc.org/ecg



Lappet-faced Vulture (Torgos tracheliotus)

In this issue

The Foundation for Analytical Science & Technology in Africa (FASTA) is a joint initiative by industrial and academic scientists to promote analytical chemistry in Africa by funding training and equipment for this continent. For example, improved analytical capability and expertise in Kenya will lead to an expansion of environmental monitoring programmes and an opportunity to protect the rich biodiversity of East Africa. Some of the participants of FASTA describe the work of this

RSC Advancing the Chemical Sciences

organisation on pp 3-8 of this issue. Declining populations of vultures, such as the Lappet-faced vulture (pictured, one of the most powerful and aggressive of African vultures) and other scavenging species are a concern in Kenya. Accidental or even deliberate misuses of pesticides are implicated in the decline of vulture colonies. One of **FASTA**'s objectives is to upgrade analytical techniques and allow the routine monitoring of forensic samples for pesticide contamination.

Also

Geochemist John McArthur from UCL and his colleagues revisit the geology of West Bengal to try to explain the subsurface distribution of arsenic which causes pollution of water supplies. Vernon Somerset from CSIR, South Africa, describes developments in voltammetric trace metal analysis. And the RSC's new Environment, Sustainability and Energy Division (ESED) is unveiled by Brian Carter.

Contents

FASTA and environmental monitoring in Kenya: 3

Arsenic distribution in groundwater: new geochemical evidence: 9

Voltammetric trace metal analysis for environmental monitoring: 13

Meeting report: 2011 ECG DGL & Symposium: 16

Forthcoming meeting: Environmental Chemistry: A Historical Perspective: 20

ESED Interest Groups: 22

Recent books at the RSC library: 24

ECG Bulletin

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

Editors

Cecilia MacLeod, Arcadis, 10 Furnival Street, London EC4A 1YH Cecilia.macleod1@btinternet.com

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

Editorial Board

Imad Ahmed, Lancaster University Stephen Ball, Leicester University Jo Barnes, University of the West of England, Bristol Bill Bloss, University of Birmingham Mic Daniel, Mirfield, West Yorks. James Lymer, Wardell Armstrong LLP, Sheffield Rupert Purchase, Haywards Heath, West Sussex Leo Salter, Cornwall

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

ECG *Bulletin* © The Royal Society of Chemistry—Environmental Chemistry Group 2011

Registered Charity Number 207890

This and previous issues of the *Bulletin* are available without charge online at www.rsc.org/ecg. Each member of the Environmental Chemistry Group also receives two issues per year of the printed ECG Bulletin. For membership details visit www.rsc.org/Membership.

Environmental monitoring in Kenya: preserving the biodiversity of East Africa

The Foundation for Analytical Science and Technology (**FASTA**) has been helping to develop analytical research facilities in African universities and improve their scope for environmental monitoring. **Steven Lancaster and colleagues** explain how an expansion of analytical capacity in Kenya benefits and encourages biodiversity in East Africa.

Introduction

The Foundation for Analytical Science & Technology in Africa (FASTA) is a registered charity comprised of industrial and academic scientists from the UK's analytical sector. It was founded by Steve Lancaster (Royal Society of Chemistry) and Barrie Nixon (Mass Spec UK) on September 20th, 2006 to support the development of promising scientists, analytical research and the preservation of the environment in Africa, via capacity-building and technology transfer. This was in response to a request for assistance from Professor Anthony Gachanja of Jomo Kenyatta University of Agriculture & Technology. Having observed a lack of analytical equipment and instrumentation, he noted that this posed an impediment to scientific progress and research in Africa. Several organisations, including: Mass Spec UK, The British Mass Spectrometry Society, The Analytical Chemistry Trust Fund, The Royal Society of Chemistry, Pan Africa Chemistry Network (PACN), Pfizer, BP and Perkin-Elmer, amongst others, have been very supportive by providing generous grants and donating equipment. Their support has been critical in allowing FASTA to set up our first partner GC-MS laboratory at Jomo Kenyatta University of Agriculture & Technology (JKUAT) in Nairobi, where Anthony is based. The PACN has also provided funding towards training courses and the purchase of instrumentation in both Nairobi and Addis Ababa, which in turn has resulted in the development of analytical centres of excellence at both locations.

The aims and objectives of **FASTA** are synergistic with the PACN initiative (to progress chemistry in Africa, recognising that analytical science is key in all areas of the chemical sciences) and are summarised below:

- To facilitate research and teaching into chemical systems/processes and environmental processes;
- To enable/facilitate the provision of accurate, affordable and accessible environmental monitoring services at the local and national level;
- To promote and encourage food analysis in order to facilitate the import and export of foodstuffs that fully conform to human health and safety standards.



Fish Eagle: one of the species affected by pesticide use in the region. Photo courtesy of Munir Virani /The Peregrine Fund.

To achieve these aims and to ensure that they are sustainable, **FASTA** is working to create a critical mass of local scientists with expertise in advanced analytical technology. This base of knowledgeable people can then respond rapidly to emerging environmental issues worldwide, with emphasis on Africa, while offering high quality analysis.

In this regard, **FASTA** is collaborating with **Professor Gachanja** and continually widening the scope of the laboratory. Since its inception, **FASTA** has invested a significant proportion of its resources into JKUAT, with the view that working closely and concertedly with a small number of facilities will ensure their success and, ultimately, that of other partner facilities. Indeed, the goal is for JKUAT, under the guidance of Professor Gachanja and the directors of **FASTA**, to become a hub for analytical science in East Africa, through technical excellence and high-level analytical equipment which can be used for analysis and training throughout the region.¹⁻³

Two GC-MS instruments are currently being used for postgraduate research and analysis of environmental samples at JKUAT. FASTA has also introduced thermal desorption equipment to be interfaced with one of the GC-MS. This will facilitate detailed atmospheric research and monitoring for a range of atmospheric pollutants. Some of the ongoing projects are: assessment of adulteration of fuels in Kenya; evaluation of quality of pharmaceuticals in the Kenyan market; monitoring and degradation of pesticides and other organic pollutants in the environment; and analysis of VOCs (volatile organic compounds) in local river water, using GC-MS. Figure 1 shows a GC-MS chromatogram of river water extract and identification of two pesticides used in coffee farms, following sample preparation and preconcentration by solid phase extraction. Through this work, JKUAT is now recognised by the Kenyan government as a centre of excellence in environmental research and analytical chemistry, and is engaged in a number of important analyses, e.g. determining presence and level of methanol in illicit (and dangerous) alcoholic beverages to resolve legal disputes. The sample throughput of a range of sample types is being facilitated by the use of a high throughput sample condenser to enable the concentration of multiple samples after extraction with

organic solvents. These include pesticide residue samples in vegetables and honey, natural products from plants and the proposed concentration of forensic samples from wildlife.

FASTA and biodiversity conservation initiatives

Addressing the current environmental contamination issues that threaten wildlife and ecosystems in Africa will necessitate bridging the theoretical gap that often exists between analysts and conservationists and encouraging these stakeholders to merge their expertise. To achieve this, FASTA and Ngaio Richards, a forensic ecologist and wildlife conservationist, are working within a network of chemists and biologists. Together, they seek to develop the sampling and analytical chemistry structure required to gather sufficient data regarding the severe decline in Kenyan scavenger populations (e.g. vultures, lions and hyenas). Ngaio Richards' doctoral research focused on the detection of nonsteroidal anti-inflammatory drugs (often abbreviated as NSAIDs) such as diclofenac (better known to arthritis sufferers as Voltarol/Voltaren) in alternative samples such as the hair of livestock animals and vulture feathers. (See Footnote 2) This research was inspired by a revelation which stunned the conservation community early in 2005, namely that vultures (Gyps species) on the Indian subcontinent were being poisoned by residues of diclofenac present in livestock carcasses.^{4,5} The drug was administered to the livestock to treat joint ailments/lameness, then carcasses were left out for the vultures to consume, and exposure induced visceral gout. So many vultures died that three species of Gyps were virtually extinguished.

Ngaio Richards approached **FASTA** in 2006 to discuss whether this research would be relevant to the analytical efforts underway to protect Kenya's ailing vulture



Figure 1: GC-MS chromatogram of a river water sample SPE extract.

population, having learned about work being undertaken by FASTA from a previous report.³ However, after she had been in contact with a number of Kenya-based biologists and conservationists, it emerged that the most pressing threat to scavenging species was in fact pesticides used deliberately as poisons. A number of pesticides have been used for this purpose with the carbamate insecticide Carbofuran being particularly effective. This has been used at an alarming rate against a number of wildlife species.^{6,7} The habitat available for wild animals is increasingly limited and most of the remaining wildlife/nature reserves are immediately adjacent to populated and/or agricultural areas. Lions may prey on livestock (which appear to them a ready and easy source of food), and, in retaliation, ranchers or pastoralists may bait a carcass with Carbofuran to poison the lion, to prevent further decimation of livestock. Vultures, hyenas and jackals, among other scavengers, also gather at carcasses and are thus unintentionally poisoned as well. Numerous incidents of mass mortality have occurred, including one in which over one hundred vultures were poisoned. Many 'nuisance' animals such as baboons are also targeted (e.g. poison is injected into bananas) because they damage crops. There is also a growing concern for human health since, in some areas, Carbofuran is used for the practice of 'pesticide hunting' and 'pesticide fishing', whereby pesticides are used to bait and capture birds and mammals or sprinkled in water, for the purposes of collecting fish, for human consumption.

Unfortunately, there is not yet an organized monitoring system in place in Kenya, nor a specific protocol tailored to preserve the forensic integrity of samples collected in the field. Advanced analytical techniques which are able to provide conclusive and rapid forensic evidence are only available on a limited basis in many African countries. In Kenya, analysis of wildlife samples (which is not routinely carried out) tends to be by thin layer chromatography (TLC) only. While this technique is sensitive and appropriate as a first step, specific confirmation by HPLC or GC-MS is then required as a follow-up. Results should also be verified/ confirmed at a second facility and there should ideally be an independent laboratory that could conduct quality assurance. Ultimately, the current situation has exposed the dearth of baseline data that exist on human and wildlife poisonings and shown the need to establish systematic and long-term monitoring of human and wildlife health in Kenya (and throughout Africa). FASTA hopes to address the need for more systematic environmental monitoring in а collaborative and concerted manner, by providing analytical support to and liaison between those engaged in such work.

Opportunities for collaboration in biodiversity conservation, environmental monitoring and capacity-building

The efforts to merge the analytical and conservation stakeholders attracted an Outreach Scholarship from the Analytical Chemistry Trust Fund, which enabled Ngaio Richards to spend 6 weeks in Kenya in the spring of 2010. The aim of this working visit was to meet face-to-face with Professor Gachanja and other key analytical researchers to explore the laboratory logistics and develop collaborations. Ngaio also spent several weeks in the field with various conservationists and researchers getting a sense of the challenges faced on-the-ground. The result was the development of a forensic field sampling protocol which is currently being reviewed by stakeholders. The protocol comprises a procedure for sampling several promising alternative matrices from carcasses (in addition to those that would otherwise be preferentially sampled if carcasses were found in good condition) and preserving samples (i.e. crop contents, stomach contents) when acute poisoning is An insect lifecycle timeline has also been suspected. developed (described below) to help estimate time since death and provide additional information to help determine whether or not poisoning was involved. (See Footnote).

If the monitoring of samples for environmental contaminants (e.g. Carbofuran) is to succeed on a long-term basis in Africa, it must essentially be self-sustaining. Although NSAIDs are not thought to represent a major threat to vultures and other scavengers in Kenya at this time, the background research on these drugs has nonetheless proven useful and will be used both advantageously and creatively. Given that NSAIDs can be administered to mask the signs of pain and inflammation, their use is closely monitored or in some cases prohibited in the horseracing industry. A collaboration is therefore under development between JKUAT and the Jockey Club of Kenya, whereby the laboratory would receive equine samples routinely collected on racing days to monitor for evidence of equine doping. Professor Gachanja is presently conducting a pilot project to integrate the NSAID detection methodology into a multi-screening process to monitor for evidence of equine doping. Protocol validation is already underway, and a student researcher is actively being sought to move the work forward. This collaboration would enable the JKUAT laboratory to generate a modest amount of revenue, which would in turn allow it to meet its operational costs and offer low cost analysis of wildlife samples to conservation bodies and other stakeholders with minimal financial resources. At the same time, there is a movement underway to comprehensively screen human and animal samples for evidence of exposure to a number of compounds of concern. This year, Ngaio and Anthony will also join forces with

several Kenya-based research and conservation bodies to through their coordinated research projects (CRPs). seek seed funding to pay for start-up costs. Professor Lalah is also interested in promoting the effective

A snapshot of recent developments in biodiversity conservation efforts in Kenya

In this section, we briefly outline a number of exciting and important initiatives that are currently underway in Kenya to conserve biodiversity and protect the environment. The directors of **FASTA** are convinced that integrating an analytical approach will greatly strengthen such initiatives and we will be pleased to offer our support as needed. This also provides us with an opportunity to showcase the outstanding efforts of our colleagues, who have managed to accomplish a great deal, often with relatively scant resources at their disposal.

Environmental monitoring and biodiversity conservation initiatives

For his MSc research, Peter Otieno, a secondary level chemistry teacher and a student at the University of Maseno, collected soil and water samples from two agricultural districts for analysis of Carbofuran residues and its primary metabolites. He also analysed the feet and beaks of several desiccated vultures that were recovered from the field. Residues of Carbofuran and/or primary metabolites were detected in all three types of samples.^{10,11} Peter's work was conducted under the direction of Professor Joseph Lalah (at Nairobi Polytechnical University) and Dr Munir Z. Virani of the US-based The Peregrine Fund and the National Museums of Kenya. Peter's current PhD research focuses on evaluating the performance of enzyme linked immunosorbent assay (ELISA) kits to assess the influence of climate change on the distribution of selected pesticide residues in sediment and water in Lake Naivasha. He will also evaluate the level of bioaccumulation of pesticide residues in fish species that are exposed to (elevated) residues levels in the aquatic ecosystem. ELISA kits are viewed by many as a viable analytical tool in monitoring and screening programs. The aim of the study is to generate accurate data that will be used to verify whether or not this is in fact the case for monitoring within the Kenyan (tropical) ecosystem.

Professor Joseph Lalah, who has recently been appointed as the Director of Research and Postgraduate understand the impacts of poisoning on vulture populations Programmes for Nairobi Polytechnical University, is also in Kenya, The Peregrine Fund and the Raptor Working involved in the development of integrated analytical approaches to assess indicators of the effectiveness of pesticide management practices at the catchment scale. For example, he is presently involved in an assessment of sugar cane farms in Nzoia area of Kenya where pesticides (particularly herbicides) are used intensively. This work is supported by the International Atomic Energy Agency

through their coordinated research projects (CRPs). Professor Lalah is also interested in promoting the effective use of selected, non-persistent pesticides in mosquito larval control and is working on this with a student. In addition, he is supervising the work of a number of postgraduate students in the area of organic contaminants and inorganic contaminants (e.g. mercury), using HPLC/GC/GC-MS. Professor Lalah wishes to encourage efforts aimed at providing capacity for analytical techniques especially with respect to wildlife protection, environmental contamination and monitoring in Kenya and is very open to the kinds of partnerships and collaborative ventures that **FASTA** is keen to foster.

The Living with Lions (LWL: www.lionconservation.org/) programme, comprised of seven researchers and 34 Masaai (the Lion Guardians, warriors see: www.lionconservation.org/lion-guardians.html) are working to find ways for lions and local people to coexist and to ensure that the benefits of lions are made more tangible to local communities. There is now a growing concern that if the current rate of poisoning continues unabated, the lion population in Kenya faces the very real possibility of going extinct within the next five years. LWL has made great strides towards increasing the tolerance of communities towards lions, however finding ways to halt the use of poisons and their repercussions to the lion population is proving very difficult. The analytical infrastructure to detect and identify compounds that pose toxicological threats to lions (and vultures, discussed below) does not yet exist within Kenya, however this is an area that FASTA and JKUAT are actively working towards with the other partners in the network.

Kenyan vultures are on the decline and face a number of threats to their populations, which in turn has severe repercussions to ecosystem integrity.¹² Dr Darcy Ogada has recently highlighted the important role played by vultures in fully decomposing carcasses.¹³ Using a series of observational and experimental trials with livestock carcasses, Dr Ogada and her colleagues found that in the absence of vultures mean carcass decomposition time more than tripled. Thus, vulture extinction could have far reaching ecological consequences and as they continue to decline due to poisoning and other human activities, increasing carcass consumption by mammalian scavengers may lead to carcasses becoming hubs of disease transmission within the scavenging carnivore community. In order to further understand the impacts of poisoning on vulture populations in Kenya, The Peregrine Fund and the Raptor Working Group of Nature Kenya, together with local wildlife conservancies, are planning a project in northern Kenya that will examine how land-use practices and human activities impact vulture populations. As part of this project, local attitudes and knowledge about vultures will be evaluated, to determine the extent livestock farmers understand the

environment. In October of this year, International Vulture lakes, where they are found in high densities. The African Awareness Day celebrations will be held in Laikipia. Three population appears to have decreased over the last two plays and songs about the importance of vultures. There will the lakes and subsequent chemical runoff into the lake conserving vultures and not using poisons. Participants will also be taken on a safari inside the conservancy to catch a glimpse of vultures in their natural habitats.

Dino Martins, an entomologist from Kenya who was recently awarded a PhD from Harvard, has been studying the repercussions of pesticides to beneficial insects, primarily honeybees/pollinators and dragonflies. Dino recently developed an insect lifecycle timeline (as far as we know, the first of its kind in Kenya)¹⁴ to assist with establishing time of death at wildlife carcasses. Since insects are usually the first of the scavengers and decomposers to arrive at a carcass, proper observations of insects and their behaviour (particularly abnormal behaviour), mortality in and around a carcass and toxicological analysis of insects recovered from the carcass and immediate vicinity can help identify or narrow the compound(s) used. Insects can also be collected for toxicological analysis, to aid in positive identification of compounds and confirm suspicion of poisoning. Dino has also examined the effects of 'pesticide fishing' on dragonfly populations in Lake Victoria.¹⁵ His colleague Martin Odino, a conservation biologist affiliated with the National Museums of Kenya, has been conducting an extensive analysis of the repercussions of 'pesticide hunting' to migrant and resident birds in rice settlement schemes.⁷

In addition, Dino (who has, incidentally, just been named an 'Emerging Explorer' by National Geographic: http:// www.nationalgeographic.com/field/explorers/dino-martins/) is looking at the direct effects of pesticides on bees in Kenya. This is currently being drafted as a review of 'routes to wild bee pesticide exposure' for the bee families Halictidae and the Carpenter bees (Apidae). Preliminary data indicate that wild bee species are exposed to pesticides and suffer many negative effects from them. Many different aspects of wild bee biology are relevant to pesticide exposure including: nesting sites in soil that receive drainage water from crop fields, social behaviour where bees share nest sites/food resources and seasonality where bees forage intensively from limited floral resources. This work will be published shortly as part of a broader review of the effects of pesticides on bees.

Masumi Gudka, a Kenyan Master's student (at the University of Cape Town/Percy FitzPatrick Institute of African Ornithology), is investigating the exposure of African fish eagles (Haliaeetus vocifer) to organochlorine compounds in Lake Naivasha and Lake Baringo under the supervision of Dr Munir Virani and Dr Rob Simmons. As top predators and a revenue-generating tourist attraction, the fish eagle is a highly emblematic species that provides important ecological and economic services to the rift valley

hundred schoolchildren will be invited to perform dances, decades at both lakes. Increased agriculture in and around also be an art competition and lectures on the importance of waters could be contributing to this decline. The objective of the study is to screen water, sediment, fish and fish eagle blood sampled for pesticides and compare chemical residues with areas in close proximity to flower farms. This study is



Pesticide exposure is monitored by studying bees and their habitat. Photo courtesy of Dino J. Martins.

important because few have considered the impact of organochlorine residues in Kenyan freshwater lakes and their supported biodiversity. Historical databases of OC residues for purposes of comparison are therefore lacking. Information on best practice sample collection and preservation are available but in tropical climates preserving sample integrity is tricky and difficult, especially without the use of on-site laboratories and facilities.

Conclusions

The JKUAT laboratory will liaise with the relevant laboratories and researchers to remain aware of developments in the conservation and analytical community. Additionally, links between FASTA and PACN are ensuring that chemists across the entire African continent are collaborating and facilitating collaboration with UK scientists. Given the wealth of experience represented, and the dedication shown, we have no doubt that we will be able to develop and implement a highly efficient and successful monitoring system in the years ahead. Colleagues wishing to learn more or contribute to any of the initiatives described in this article or to offer analytical expertise and other means of support are invited to contact Steve Lancaster and Ngaio Richards.

References

- 1. S. Lancaster, Mass Matters, 2006, 51,11.
- 2. S. Crossland, Mass Matters, 2006, 52, 6.
- 3. N. Richards and S. Lancaster, Mass Matters, 2007, 54, 6.

Meteyer, B. A. Rideout, H. L Shivaprasad, S. Ahmed, M. J. University of Cape Town, Rondebosch 7701, Cape Town, I. Chaudhry, M. Arshad, S. Mahmood, A. Ali, and A. A. South Africa Khan, Nature, 2004, 427, 630-633.

5. N. Richards, Chemistry & Industry, February 28th, 2008.

6. C. O'Driscoll, Chemistry & Industry, January 28th, 2008.

7. M. Odino and D. L. Ogada, Report to the Bird Committee of Nature Kenya, 2008.

8. N. L. Richards, G. Cooke, V. Simpson, S. Hall, N. M. Harrison and K. S. Scott, European Journal of Wildlife Research, 2011, DOI 10.1007/s10344-011-0513-2.

9. N. Richards S. Hall, K. Scott and N. Harrison, Environmental Pollution, 2011, 159, 1446.

10. P. O. Otieno, J. O. Lalah, M. Z. Virani, I. O. Jondiko and K.-W. Schramm, Journal of Environmental Science and Health, 2010, 45, 137.

11. P. O. Otieno, J. O. Lalah, M. Z. Virani, I. O. Jondiko and K.-W. Schramm, Bulletin of Environmental Contamination and Toxicology, 2010, 84, 536.

12. M. Z. Virani, C. Kendall, P. Njoroge and S. Thomsett, Biological Conservation, 2011, 144, 746.

13. D. L. Ogada, M. E. Torchin, V. O. Ezenwa and M. Kinnaird, Conservation Biology, in press.

14. D. J. Martins, Generalised protocol for sampling insects from carcasses in East Africa. Insect Committee of Nature Kenya - The East Africa Natural History Society. Nairobi, Kenya, 2010, Informally distributed to stakeholders

15. Martins, D. J. Differences in Odonata abundance and diversity in pesticide-fished, traditionally-fished and protected areas in Lake Victoria, Eastern Africa (Anisoptera). Odonatologica, 2009, 38, 247.

STEVEN LANCASTER,¹ NGAIO L. RICHARDS,^{1,2,3} ANTHONY GACHANJA,^{1,4} DARCY OGADA,⁵ MASUMI GUDKA,⁶ JOSEPH LALAH,⁷ PETER OTIENO,⁸ MUNIR Z. VIRANI,^{5,9} DINO J. MARTINS^{10,11}

¹Foundation for Analytical Science & Technology in Africa, St Ives, Cambridge, UK, PE27 3YN

²Working Dogs for Conservation, 52 Eustis Road, Three Forks, Montana, USA 59752

³Investigative Chemistry Research Group, Department of Life Sciences, Anglia Ruskin University, East Road, Cambridge, UK CB1 1PT

⁴Chemistry Department, Jomo Kenyatta University of Agriculture & Technology, P.O. Box 62000, 00200 Nairobi, Kenya

⁵The Peregrine Fund, 5668 West Flying Hawk Lane, Boise, Idaho 83709, USA

4. J. L. Oaks, M. Gilbert, M. Z. Virani, R. T. Watson, C. U. ⁶The Percy FitzPatrick Institute of African Ornithology,

⁷Department of Chemical Sciences and Technology, School of Applied Sciences and Technology, Kenya Polytechnic University College, P.O. Box 52428-00200 City Square, Nairobi, Kenya

⁸Department of Chemistry, Maseno University, P.O Box 333, 40105, Maseno, Kenya

⁹Ornithology Section, Department of Zoology, National Museums of Kenya, P.O. Box 40658-00100, Nairobi, Kenya

¹⁰Insect Committee of Nature Kenya, National Museums of Kenya

¹¹Turkana Basin Institute – Stonybrook University, N507 Social and Behavioural Sciences, Stony Brook, New York, USA 11794-4364

FOOTNOTES

1. The Investigative Chemistry Research Group is currently assessing the presence of NSAIDs in indicator species in the aquatic and terrestrial environment, see references 8 and 9.

2. Ngaio Richards was also in Kenya to conduct research and interviews for a book she is editing on the global repercussions of the carbamate insecticide, Carbofuran, on wildlife populations. The royalties of this book will be placed in a research fund to further the analytical and conservation work underway, in partnership with JKUAT and FASTA.

WEB LINK

http://www.chemistry.manchester.ac.uk/groups/pob/ fasta/

How sea level and ancient soils control the distribution of arsenic pollution in groundwater

The detrimental health effects of arsenic-contaminated drinking water have once again hit the headlines, with the publication in early 2010 of a comprehensive epidemiological study of the effects of As in drinking water. The study shows that the effects may be worse than feared, making it even more urgent to understand what controls the distribution of As in the subsurface as a prelude to mitigation of pollution in water supplies and the future safe development of affected aquifers. In early 2009, we reported on a new hypothesis that might explain that distribution; it had been proposed by researchers of the London Arsenic Group (LAG). Here we report on the first test of that hypothesis, as explained by **Professor John McArthur** of UCL and a member of LAG.

River sediments and aquifers

Sediments are laid down along the lower stretches of rivers as they slow their rate of flow, and in deltas where the rivers are stopped short by the sea, and so deposit their sediment load. The sediments are often sandy or silty, and so are not just porous but also permeable. The water within the pores may be of a quality fit for domestic use, and be pumped out, or bailed out in a well, from the sediments that are therefore termed an 'aquifer'. Aquifers laid down by rivers are termed 'alluvial', or 'deltaic' if they happen to form a river delta. As deltas and river banks were amongst the first places on Earth to be colonized, and host many of the world's major cities, groundwater from alluvial aquifers worldwide provides a good proportion of the world's supply of drinking water. The source is particularly important in SE Asia, where many regions have a dry season e.g. the Ganges/ Brahamaputra delta region.

Arsenic pollution of groundwater. Throughout history, mankind has known that digging a hole in the ground is a good way to obtain water. If that water tasted good, it was assumed safe for public supply. This notion was coming under sporadic fire after 1950, but as late as 1970 was still prevalent. The belief led to the promotion, especially in Bangladesh and West Bengal, of the use of groundwater as a safe alternative to microbiologically-polluted surface water for domestic supply. But by the late 1980s, suspicion had

arisen in West Bengal that the water might be polluted with As, so a wide-ranging report on the matter was prepared (PHED 1991). Even so, the matter was largely ignored until Dipankar Chakraborti, of Jadavpur University in Kolkata, West Bengal, raised the lid off the boiling pot by arranging a conference on the issue in 1995. As a consequence of the conference, money was made available by the UK's ODA for a survey of groundwater across much of south and central Bangladesh, the country thought most affected. The survey found that around 25% of wells contained > 50 μ g/ As, the local water quality limit, whilst half contained more that 10 µg/As, the maximum recommended by the World Health Organization. Since 1995, the problem of As pollution has revealed that the pollution is severe and global in extent, affecting at least 30 deltaic and coastal aquifers worldwide (Ravenscroft et al., 2009 and references therein).

The harm being done. In the deltaic aquifers of SE Asia, concentrations of As are commonly 50 to 200 μ g/L and values up to 4,000 μ g/L have been recorded. Arsenic dissolved in groundwater in these amounts is odourless, tasteless, poisonous, and carcinogenic. At such concentrations, its poisonous effects take years to show. Which is why in 2000, Alan Smith, epidemiologist at UC Berkley, wrote that the As-pollution of groundwater in Bangladesh was "the worst mass poisoning of a population in history". He predicted that, if those drinking water containing > 500 μ g/L of As continued to do so, by 2010,

one in ten of their deaths would be arsenic-related. Now, in 2010, the results have been published of an epidemiological study of consumers in Araihazar, an As-polluted region of east-central Bangladesh. The study, by staff of Chicago and Columbia Universities, has made the significant claim that, in a cohort of 11,746 individuals studied for 10 years, "an estimated 21% of all deaths, and 24% of deaths associated with chronic disease, could be attributed to arsenic exposure (>10 μ g/L) in drinking water." The figures are more alarming even than Alan Smith's dire prediction for 2010.

Distribution of arsenic pollution. The mechanism of As pollution was revealed in 1998. But what controls the patchy distribution of As-pollution is less clear. That sea level has exerted an influence on both the vertical and lateral distribution of As pollution was shown by Peter Ravenscroft, and his team at Mott MacDonald International in Dhaka and the University of Dhaka (in DPHE 1999). They showed that the As pollution was confined to sediments laid down after a low-stand of sea level that occurred around 20,000 years ago. That was the most recent of many times at which the world's ice-caps reached a maximum extent, so the time is termed by geologists the **Last Glacial Maximum (LGM**; \approx 20,000 years BP). Ravenscroft showed that wells drawing water from

sediments deposited as sea level rose after the LGM were likely to be polluted by As. Those, mostly deep wells (>150m deep) that drew water from older sand deposited before the LGM were As free.

The palaeosol model of arsenic pollution

An hypothesis to explain the distribution of As-pollution in the Bengal Basin. Ravenscroft's team explained the distribution of As-pollution at the 10-to-100 km scale, but not the pronounced inhomogeneity found at lesser scales. Developing Ravenscroft's ideas, an hypothesis reported on in the ECG Bulletin in early 2009 (McArthur et al., 2008) did just that. The model proposed that as sea level fell by about 120 m, as the last ice-age developed to its maximum between 125 ka and 20 ka (at the LGM), the exposed coastal areas were subject to subaerial weathering. Rivers incised into the exposed coast to maintain their base levels, and the exposed regions between the rivers, termed the interfluves, weathered and developed a capping of impermeable clay soil, termed a palaeosol. Underlying sands were weathered, as groundwater flowing through them to oxidise Fe(II)bearing detrital minerals and turn the sands brown from the iron-oxides produced. This weathered, oxidized, and eroded,



Figure 1: The field area. Base map is 1-inch toposheet of West Bengal circa 1975. Geographic reference system used is WGS84 in degrees and decimal minutes. Key in upper left. a. Concentrations of As in well water. Solid black line encloses area where As in groundwater is $\leq 10 \mu g/L$, and drilling proved the LGMP to be present. Southern dotted, black, extensions outline the area where erosion has cut out the palaeosol but left underlying Late Pleistocene brown sands largely undisturbed. b. Drilling sites for proving subsurface sedimentology.



Figure 2: The colour of well-stain: a. Black colouration of a well, well-screen, or domestic utensils, derives from precipitation from groundwater of manganese oxide and indicates that a well is As-free and, in southern West Bengal, also that it is screened in the shallow aquifer. b. Red colouration derives from precipitation from groundwater of iron oxide and indicates the presence of As > 10 μ g/L in shallow wells.

landscape, capped by the LGMP (Last Glacial Maximum Palaeosol), was buried by later (post LGM) sediments as sea level rose between 20 ka and 6 ka to near its present level. The rise pushed the sea-shore landward, backed up the rivers, and made them deposit their sediment load so as to build the modern delta we call the Bengal Basin (Bangladesh and West Bengal). The key postulate of the 'palaeosol model' is that the weathering of interfluves between 125 ka and 20 ka capped the oxidised Pleistocene brown sands with an impermeable palaeosol, termed the Last Glacial Maximum Palaeosol (LGMP). The LGMP would have formed regionally, if discontinuously, and so should strongly influence groundwater flow, thus controlling the distribution of As-pollution. It would do so by preventing access to underlying aquifers of As-pollution from overlying groundwater, or access of dissolved organic matter that could reduces As-bearing sedimentary iron oxides and so release As to groundwater.

Testing the palaeosol model of As-pollution. The model was developed for an area in West Bengal that was less than 1 km^2 . Members of LAG were aware that it had to be demonstrated to apply more widely before it would gain acceptance worldwide, so they set out to test the models predictions over a bigger area. The London Arsenic Group has now tested that model across 102 km^2 of southern West Bengal and found that it could not falsify the hypothesis – so it passes its first test.

The predictions were that were that where the LGMP was found in the subsurface, the underlying aquifer would be As -free, and that where As-pollution was found, the LGMP would be absent. And that is just what they found. In the subsurface under 47 km² of contiguous country in which well water was As-free, drilling proved the existence of the LGMP capping brown sand aquifers (a palaeo-interfluve setting), as predicted by the palaeosol model (**Figure 1**). In flanking regions, where concentrations of As in well water mostly exceed 50 μ g/L, drilling proved the absence of the LGMP and that the aquifer consisted of grey palaeo-channel sands. Their results appear to validate the palaeosol model across 102 km2 of the study area. The LAG group are now keen to test that model over a larger area, in other localities.

Mapping As-pollution with well-colour. McArthur's team also came up with a surprise. Although it was known that As-polluted water was rich in dissolved Fe (up to 30 mg/L) and that unpolluted water was often rich in Mn (up to 9 mg/ L), no one before had taken much notice of the fact that precipitation of these elements as oxides gave different colours to wells: iron oxide-coloured wells red; manganese oxide-coloured wells black, as water regularly spilt and splashed over the well and its concrete surroundings (Figure 2). By applying this basic observation in a predictive way, the team was able to map As-polluted (palaeo-channel) areas and As-free (palaeo-interfluvial) areas with unprecedented speed without even analyzing wells for As. Checks using As analysis revealed a prediction rate that was 94% successful for As-free wells and 86% successful for As -polluted wells - and might have been better if, like some 10% of the male population, McArthur did not suffer from a degree of colour blindness.

Palaco-interfluvial aquifers: consequences for water supply. Where it is present, the LGMP, which is effectively impermeable, protects the underlying palaeo-interfluvial



Figure 3: The conceptualization of the risk of As-pollution in palaeo-interfluvial aquifers in terms of travel times for As. Note the logarithmic horizontal scale. Groundwater flow rate is 30 m per year at palaeo-interfluvial margins. The impermeable palaeosol prevents vertical recharge to palaeo-interfluves, so recharge moves laterally from flanking palaeo-channels, losing As by sorption as it does so. Note that the LGMP affords protection to the palaeo-interfluvial aquifer against ingress of any mobile pollutants, including nitrate, pesticide, DNAPL and NAPL, not just against ingress of natural As-pollution.

aquifer from downward migration of mobile pollutants, such as arsenic, nitrate, pesticides, NAPLs and DNAPLs, The LGMP diverts recharge to flow laterally to palaeo-channels, from where it flows downward and then laterally into the palaeo-interfluvial aquifers. The As in this recharging water is stripped from the groundwater by sorption onto the sedimentary iron oxide in brown sands (Figure 3). The palaeo-interfluves thus act as giant, in situ, As-removal filters. The impermeable LGMP, and the sorptive capacity for As of the brown palaeo-interfluvial aquifers, together provide a dual protective barrier against As-pollution. The retardation factor applicable to the lateral migration of As into the palaeo-interfluvial aquifers has been estimated to be between 10 and 300 - a large range in need of refinement. But given these extremes, the As-free palaeo-interfluve mapped by LAG is, over all by its peripheral margin, safe from the threat of As pollution for decades to hundreds of years (Figure 3).

Literature cited

McArthur, J. M.; Ravenscroft, P.; Bannered, D. M.; Milo, J.; Hudson-Edwards, K. A.; Sengupta, S.; Bristow, C.; Sarkar, A.; Tonkin, S.; Purohit, R. How paleosols influence groundwater flow and arsenic pollution: a model from the Bengal Basin and its worldwide implication. *Water Resour. Res.*, 2008, **44**, W11411, doi:10.1029/2007WR006552.

Ravenscroft, P.; Brammer, H.; Richards, K. S. Arsenic Pollution: A Global Synthesis. Wiley-Blackwell, 2009.

DPHE; Groundwater Studies for Arsenic Contamination in Bangladesh. Final Report, Rapid Investigation Phase. Department of Public Health Engineering, Government of Bangladesh. Mott MacDonald and British Geological Survey (6 vols.), Dhaka, 1999.

PHED: National Drinking Water Mission Project on Arsenic Pollution in Groundwater in West Bengal. Final Report, Steering Committee, Arsenic Investigation Project, PHED, Kolkata, Govt. of West Bengal, India, 1991, 57 pp.

Argos, M.; Kalra, T.; Rathouz, P. J.; Chen, Y.; Pierce, B.; Parvez, F.; Islam, T.; Ahmed, A.; Rakibuz-Zaman, M.; Hasan, R. *et al.* Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study. *Lancet*, 2010, **376**, 252–258.

McArthur, J. M.; Banerjee, D. M.; Hudson-Edwards, K. A.; Mishra, R.; Purohit, R.; Ravenscroft, P.; Cronin, A.; Howarth, R. J.; Chatterjee, A.; Talukder, T. *et al.* Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem.*, 2004, **19**, 1255–1293.

McArthur, J. M.; Banerjee, D. M.; Sengupta, S.; Ravenscroft, P.; Klump, S.; Sarkar, A.; Disch, B.; Kipfer, R. Migration of As, and ${}^{3}\text{H}/{}^{3}\text{He}$ ages, in groundwater from West Bengal: implications for monitoring. *Water Res.*, 2010, **44**, 4171–4185.

JOHN McARTHUR

Department of Earth Sciences, University College London, Gower Street, London UK WC1E 6BT

Home page: www.es.ucl.ac.uk/people/mcarthur/

London Arsenic Group: www.es.ucl.ac.uk/research/lag/as/

Environmental monitoring using voltammetric trace metal analysis

The need to refine and develop analytical tools for use in field surveys of heavy metals in the environment has been a long standing desire for analytical and environmental chemists. **Dr Vernon Somerset** from the Council for Scientific and Industrial Research (CSIR), South Africa, reports on new developments in voltammetry which have revived the application of this technique for environmental field mapping and monitoring.

Monitoring trace metals in the environment

Concentrations of heavy metals (and some organic contaminants) are increasing in parts of the environment as a result of anthropogenic activity. For metal contamination, particular attention has been paid to the rapid diffusion and speciation of heavy metals in the environment. As a consequence, many novel methods for the determination of metals at trace and ultratrace levels have been introduced. Metal contaminants tend to concentrate in aquatic matrices such as suspended matter, sediment and biota - resulting in their presence in the aquatic food chain. In turn, there is an increasing risk to human health if vegetables, fruit and meat with high levels of metal contaminants are consumed. Therefore, the continuous assessment and monitoring of trace metals in the environment is essential to gain a better understanding of the individual and interactive effects of the trace metals in water resources (rivers, lakes, dams, reservoirs). National and international legislation set limits on the maximum allowable concentrations of trace metals in the air, water, and aquatic ecosystems. In order to regulate environmental legislation, routine measurements of metals in the environment are needed to assess compliance by different organisations, businesses, and industries. Monitoring and measurements also require accredited sample collection and analytical procedures. Setting the standard, and assessing the compliance to the standard, is important and allows for an accredited assessment of the environment (Somerset, 2009; Locatelli and Torsi, 2001).

Various established and accurate methods exist for the simultaneous analysis and determination of metal ions at trace levels. Instrumentation for these methods encompasses inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), atomic absorption spectrometry (AAS), and atomic fluorescence spectrometry (AFS), coupled to a range of detectors for specific problematic contaminants. These methods are highly efficient, but they require tedious sample pre-treatments, highly qualified technicians and sophisticated instruments. Also, they can be time consuming and are not suitable for field analysis of multiple samples (Somerset *et al.*, 2010; Cauchi *et al.*, 2008; McGaw and Swain, 2006). Stripping voltammetry has emerged as an alternative and robust technique for trace metal analysis of environmental samples.

Stripping voltammetry

The use of stripping voltammetry as a technique for metal determination at trace levels has increased in popularity over the last decade, with various electrode configurations now available to perform the analyses. The effectiveness of this technique can be attributed to the remarkable sensitivity of stripping voltammetry and its multi-element and speciation capabilities, coupled with low cost and suitability for on-site measurements (Locatelli and Torsi, 2001). Furthermore, electrochemical stripping analysis has been successfully established as a trace analysis technique for more than three decades. During this time many advances have been made in different areas of the technique with specific emphasis on various electrode assemblies for assorted contaminants.

Stripping analysis is an electro-analytical technique and makes use of a two-step approach, consisting of a "preconcentration" step of the analyte on the surface of a working electrode. This is followed by the detection step where the metals are stripped away from the electrode during an appropriate potential scan. The accumulated analyte is normally detected and quantified using voltammetric or chronopotentiometric techniques. Stripping analysis provides useful information on the total metal content of a sample matrix, but also allows characterisation of the metal ion in its different chemical forms, where applicable (Economo, 2010).

Stripping voltammetry combined with disposable sensors, manufactured using screen-printed technology, has become very popular in the last two decades because of its simplicity, affordability, and ease-of-use. This process involves the sequential deposition of layers of different conductive or non-conductive inks on a variety of inert substrates. Screen-printed carbon electrodes (SPCEs) in stripping voltammetric techniques allow a high degree of sensitivity and selectivity in metal ion determination. The production of screen-printed electrodes has enabled the mass production of disposable electrodes, and is a promising route for inexpensive and yet highly reproducible chemical sensing devices (Somerset *et al.*, 2010; Palchetti *et al.*, 2005).

In **Figure 1**, a screen-printed sensor is connected to a potentiostat or integrator. The resulting stripping voltammogram can further be interpreted to determine the concentration of the analyte of interest. The use of screen-printed electrodes (SPEs) has simplified the *in situ* analysis

of environmental samples for heavy metals. Samples may also be screened on site before they are taken to the laboratory for further analysis. Because the SPEs can be connected to portable and compact (hand-held) batteryoperated stripping analysers, commercialisation of these devices is advancing, and several models now allow the detection of metal ions in environmental samples.

14

Continuing technological changes in electrochemical sensor techniques will play an important role in the development of sensor detection systems for the analysis of environmental samples and other materials. The introduction of nanomaterials is another factor that will contribute to advances in electrochemical devices. Furthermore, progress in microelectronic and microfluidic technologies has permitted the miniaturisation of analytical systems. This in turn reduces energy requirements and sample volumes, resulting in reduced reagent consumption and waste generation, leading to increasing sample throughput (Farre *et al.*, 2009).

Conclusion

The demands for rapid, reliable and inexpensive sensors for the measurement of metals in biomedical, environmental, and industrial samples in the last decade have resulted in the introduction of new techniques in stripping voltammetry. With improvements in detection, the adoption of stripping analysis for environmental monitoring has much to offer analytical and environmental chemists.



Figure 1: Scheme of a screen-printed sensor that can be connected to a potentiostat, when in operation will deliver a stripping voltammogram that is used to determine the concentration of an analyte(s) in a sample matrix.

References

Cauchi, M., Bessant, C., Setford, S. 2008. Simultaneous quantitative determination of cadmium, lead, and copper on carbon-ink screen-printed electrodes by differential pulse anodic stripping voltammetry and partial least squares regression. *Electroanal.*, **20**(23): 2571-2577.

Economo, A. 2010. Review: Recent developments in on-line electrochemical stripping analysis – An overview of the last 12 years. *Anal. Chim. Acta*, **683**: 38-51.

Farre, M., Kantiani, L., Perez, S., Barcelo, D. 2009. Sensors and biosensors in support of EU Directives. *Tr. Anal. Chem.*, **28**(2): 170-185.

Locatelli, C., Torsi, G. 2001. Voltammetric trace metal determinations by cathodic and anodic stripping voltammetry in environmental matrices in the presence of mutual interference. *J. Electroanal. Chem.*, **509**: 80-89.

McGaw, E.A., Swain, G.M. 2006. A comparison of borondoped diamond thin-film and Hg-coated glassy carbon electrodes for anodic stripping voltammetric determination of heavy metal ions in aqueous media. *Anal. Chim. Acta.*, **575**: 180-189. Palchetti, I., Laschi, S., Mascini, M. 2005. Miniaturised stripping-based carbon modified sensor for in field analysis of heavy metals. *Anal. Chim. Acta*, **530**: 61-67.

Somerset, V. 2009. Notes from the Southern Trace Metals Monitoring Network Group on Facebook, administered by V. Somerset. www.facebook.com, available in November 2009.

Somerset, V., Leaner, J., Mason, R., Iwuoha, E., Morrin, A. 2010. Development and application of a poly(2,2'-dithiodianiline) (PDTDA)-coated screen-printed carbon electrode in inorganic mercury determination. *Electrochim. Acta*, **55**: 4240-4246.

VERNON SOMERSET PhD

Senior Researcher, Water Ecosystems and Human Health, Natural Resources and the Environment, CSIR, PO Box 320, Stellenbosch, 7599 South Africa

Email: vsomerset@csir.co.za



2011 ECG Distinguished Guest Lecture, Burlington House, March 9th

Leo Salter (left) and Bill Bloss (right) present the 2011 ECG Distinguished Lecturer Medal to **Pro**fessor James Galloway from the University of Virginia. (Meeting report: pp 16-19).

Meeting report

2011 Environmental Chemistry Group Distinguished Guest Lecture and Symposium

The Nitrogen Cycle – in a fix?

The Environmental Chemistry Group held its annual Distinguished Guest Lecture & Symposium on March 9th 2011 at the RSC Chemistry Centre, Burlington House. The theme for the meeting was the effect on man and the environment of nitrogen speciation and utilisation. Around 50 delegates listened to four presentations, including the 2011 Distinguished Guest Lecturer, **Professor James Galloway** from the University of Virginia.

Dr Mark Sutton (Centre for Ecology and Hydrology, Edinburgh) opened the meeting with a talk on the *Atmospheric Nitrogen Cycle and Climate*. As a result of the development of a catalytic high pressure synthesis of ammonia from atmospheric nitrogen (Haber-Bosch process) early in the twentieth century,

"Fifty percent of the people who are alive today are alive because of the food generated from fixed nitrogen."

However, the (unintended) consequence of man-made nitrogen fixation has been the enhanced impact of nitrogen in its various oxidation states $-N_2O_1$ NO_x , NH_3 , and NO_3^- – on the environment. For example, increased eutrophication of terrestrial and aquatic systems and changes in global acidification may both be attributed to higher levels of nitrogen species in the environment. Additionally there are links between reactive nitrogen species and changes in greenhouse gas concentrations.

In order to assess the interaction of

atmospheric nitrogen and carbon 2. cycles and their impacts on climate, particularly from a European • perspective, a collaborative European project - the NitroEurope Integrated Project (http:// 3. www.nitroeurope.eu/) - has been established. Across the continent, a series Flux and Manipulation Networks - thirteen supersites, nine 4. regional sites, fifty inferential sites, twenty-two core manipulation sites, and fourteen associated manipulation sites – has been set up in forest, arable land, grassland and wetland areas to measure atmospheric N deposits (e.g. by measuring [HNO₃] μ g m⁻³). Data on regional NO₃⁻, NH₃, NH₄⁺, HNO₂ and NO₂ levels in these different habitats have been collated and the results used to estimate, for example, the effect of nitrogen on carbon sequestration and storage in forests. The NitroEurope project has led to a number of recommendations for changes in how nitrogen is utilized:

1. Agriculture

- Improve nitrogen use efficiency in crop production;
- Improve nitrogen use efficiency in animal production;
- Increase the fertiliser nitrogen equivalence value of animal manure.

(Balanced fertilisation will reduce nitrogen consumption, and changes in the way animal manure is applied and incorporated into fertiliser will reduce ammonia emissions).

Target Industry

- Reduce combustion emissions and increase energy efficiency.
- Waste water treatment
- Remove N and P.
 - Human
- Energy saving;
- Reduced consumption of animal protein;
- International communities need to work together more effectively; choice and behavioural change provide major opportunities . . . and the amount of animal products consumed by individuals must be reduced.

In the second presentation, **Professor Tim Jickells** (School of Environmental Sciences, UEA) spoke on *Atmospheric Nitrogen Inputs to the Marine Environment.*

As visualised from orbiting satellites, the colour of the earth's oceans reveals chlorophyll distribution and is hence a map of phytoplankton distribution. All productivity in oceans is driven by marine phytoplankton, which needs N, P, Si, Fe and light to survive and multiply. Sources of oceanic nitrogen inputs are summarised in the Table (see p 17).

Surveys of the oceans reveal the extent and complexity of nitrogen speciation in the marine environment. Sampling is carried out from the RRS James Cook



RRS James Cook

(pictured) in the Atlantic and on island sites (e.g. at the Cape Verde Atmospheric Observatory).

Current work carried out primarily through the 'Atlantic Meridional Transect' cruise series (AMT; http:// www.amt-uk.org/) shows high phytoplankton productivity in northern waters (due to deposition of European/US N-rich emissions), but low productivity near the equator (influenced by African emissions) and low productivity in Southern Oceans.

There are three main components of nitrogen inputs: (a) NO_x/NO₃⁻, (b) NH₃/NH₄⁺ and (c) organic nitrogen compounds (with a significant urea component). Atmospheric organic nitrogen is operationally defined as water-soluble nitrogen in rain (or aerosols) that is not present as nitrate or ammonium ions. Carbon isotope evidence suggests that the carbon component is of terrestrial plant origin, which is consistent with other studies. Organic N is an important component of total nitrogen deposition and is partially bioavailable. The inorganic nitrogen sources are dominated by terrestrial anthropogenic emissions (in 1860 total fixed nitrogen deposition to the ocean is estimated as 20 Tg N yr⁻¹ (29% anthropogenic) compared to 67 Tg N yr⁻¹ in 2000; 81% anthropogenic). Atmospheric fixed nitrogen inputs to the oceans produce 0.25 Pg C yr⁻¹uptake increase which should be

compared with the IPCC estimated net ocean uptake of 2.2 ± 0.5 Pg C yr⁻¹.

Nitrogen in the atmosphere and in oceans was the theme for the first half of the meeting. In the third presentation, **Professor Brian Chambers** (ADAS) turned attention to terrestrial effects with a talk on *Optimising Nitrogen Use Efficiency in Agriculture.*

Production of fixed nitrogen (100 million tonnes per annum) uses 2 % of the world's total energy demands and feeds 30 % of the population. Reactive Nitrogen in the environment has doubled since the introduction of fixed nitrogen and the challenge for the 21st Century is to provide an adequate quantity of healthy food for the expected 9-10 billion world population without damaging the environment.

The soil mineral nitrogen (SMN) pool is chiefly in the form of inorganic N (NH_4^+ and NO_3^-) and receives nitrogen from manures, atmospheric deposition, and fertilisers. It releases nitrogen *via*

denitrification, NH_3 volatilisation, and crop production. SMN is 'crop available' nitrogen – but this is susceptible to leaching which in turn is affected by complex seasonal factors. Hence the soil nitrogen cycle can be considered as a "leaky pipe" from which NH_3 , N_2O , NO_x and N_2 are emitted into air and NO_3^- , NH_4^+ , and dissolved organic nitrogen is released into water.

The correct fertiliser application rate is important to minimise nitrogen leaching and optimum N-fertiliser application recommendations are made on a farm-by-farm basis. However, typically 20% of recommendations are too low (low yields) and 20% are too high (wastes money, increases leaching). So can recommendations be improved?

Farm nitrogen management goals are to meet the nitrogen demands of crops/animals, to maintain a productive soil and to avoid damage to the environment. The best management practices are to use a fertiliser recommendation system (DEFRA, Planet Software, FACTs (Fertiliser Advisers Certification and Training Scheme) qualification) and to use the correct fertiliser type. Nitrogen fertilisers are estimated to be responsible for around 16% of UK ammonia emissions from agriculture. In Britain over the last 25 years manufactured fertiliser use has declined 25% for N and 45% for P due to improved efficiency of application by farmers. Urea

Nitrogen Inputs to the Oceans	Tg N yr ⁻¹
Fluvial	50-80
Atmospheric	67
Nitrogen Fixation	600-200
Lightning	< 6

fertiliser use has doubled since 1998 and ammonia emissions from urea are significant. This is being tackled by using urease inhibitors (e.g. Agrotain). Under normal conditions 24% of urea N is released to the atmosphere as NH₃, which reduces to 7% when a urease inhibitor is present.

However, it is livestock manures that are the main cause of controllable nitrogen pollution and part of the solution is to manage manures to increase nutrient use efficiency (cattle housing and slurry storage are sources of NH3 and land spreading is a source of ammonia and nitrate). The nitrogen in livestock manures is present in two forms: readily available nitrogen (rapid uptake) and organic nitrogen (slow (months/years) uptake). Nitrogen losses occur through two main pathways: rapid ammonia volatilisation and nitrate leaching.

The Manure Nutrient Evaluation Routine (MANNER-NPK) is a decision support system designed to minimise NH₃ losses to air. Different techniques for spreading manure make a huge difference to ammonia losses, for instance, slurry band spreading/shallow injection equipment minimise ammonia losses and odour nuisance, improve manure and user efficiency, and reduce environmental damage, but at a high capital equipment cost. Nitrate leaching losses following manure applications to soils depend on the season (e.g. for free draining soils: Sept. 20% loss, Oct. 17%, Nov. 10%, Dec. 5%, Jan. 3%).

By identifying Nitrate Vulnerable Zones (NVZs), the EU Nitrates Directive tackles pollution (e.g. eutrophication) of waters caused by nitrogen from agricultural sources and establishes limits for surface or ground waters (50 mg/litre of nitrate). In the UK, NVZs cover 68% of agricultural land (62% after appeal by farmers). The EU would like the UK to declare the whole country as NVZ. Most monitoring sites show stable or decreasing nitrate contamination. In NVZs organic manures are limited by a livestock manure N farm limit (170 kg/ha – stocking ratio limit), an organic manure N field limit (250 kg/ ha total N) and 'closed' spreading periods (e.g. slurry and poultry manure 1st Aug – 31st Dec only for arable farms on sandy/shallow soil).

Brian's three closing recommendations for interventions of maximum impact were to increase farm slurry storage, to encourage investment in band spreading, and to ban urea fertiliser (unless an inhibitor has been added).

Following these three presentations, **Professor James Galloway** (University of Virginia) gave the ECG Distinguished Guest Lecture for 2011 - Nitrogen: a Story of Food, Feed and Fuel. He commenced by noting the challenge of converting nitrogen in the atmosphere into a usable form - 10 million biological species need nitrogen to survive and only 1000 species can convert it to a reactive form (Nr), so nitrogen is the limiting nutrient for many ecosystems. There are two sources of Nr – by biological fixation (BNF) and by humans: fossil fuel combustion and the Haber-Bosch (H-B) process (induced BNF).

Professor Galloway identified nitrogen use as a 'wicked' problem (see *Tackling Wicked Problems: Through the Transdisciplinary Imagination*, eds. V. A. Brown *et al.*, Earthscan, 2010). Nitrogen is a "wicked" problem not a "tame" problem and one aspect of tackling such problems is by education. Which poses the question "How can chemists educate the population about nitrogen issues?"

In 1850 the world population was 1.6 billion and sources of nitrogen included lightning, BNF, guano, nitrate and cultivation. By 2005 this had changed dramatically: fossil fuel (25 Tg N yr⁻¹), cultivation (40 Tg N yr⁻¹), H-B fertiliser (100 Tg N yr⁻¹), industrial (23 Tg N yr⁻¹), and natural (50 Tg N yr⁻¹).

In 1850 nitrogen uses were for grain, meat, energy and the nitrogen cycle was different from now - human activities had limited (but not zero) influence on nitrogen deposition. But by the mid-1990s increased demand for grain, meat and energy changed the nitrogen cycle, the H-B process creates 100 million tonnes of fixed nitrogen from the atmosphere each year and fossil fuel contributions doubled; and nitrogen deposition changed to become more global with more hotspots. Humans need 13 Tg N, consume 30 Tq N but create 140 Tq N because of the 'leaky pipe'; 20% of N used in crop production enters someone's mouth but the rest is lost to the environment (only 10% of N used in animal production is "eaten".) The average adult consumes 5 kg N yr⁻¹ but needs only 3.

One environmental consequence of the increased nitrogen use is the creation of hypoxic and eutrophic coastal areas; these are largely areas linked to populations and food and the major input of nitrogen to oceans is via deposition. However, tracking the distribution of Nr distribution is difficult. For instance, a third of nitrogen produced was exported from one continent to another (31 Tg N fertiliser, 11 Tg N Grain, 0.7 Tg N Meat). And, importantly the price paid for imported food doesn't pay for the environmental damage caused in the producer country by (say) nitrogen pollution.

There is too much nitrogen and too many consequences – for instance, fossil fuel combustion produces smog, acid rain, particulate matter, forest, die-back, water acidification, eutrophication, hypoxia of fresh and

marine water, and an impact on global warming and ozone concentrations. One nitrogen atom can contribute to each of these environmental changes in sequence – the "Nitrogen Cascade".

The overall goal is to optimise nitrogen's benefits and minimise the problems and to tackle this man needs to control fossil fuel consumption, increase nitrogen uptake efficiencies in crops and animals, manage manure (fertiliser uptake, feed retention) and improve sewage treatment. This could give a 25% decrease in Nr release to environment. In order to do this the public has to be engaged with the issues because human actions control Nr introduction into the environment.

N-Print (http://n-print.org/) is a tool to estimate Nr loss to the

environment due to food, energy and materials and it asks about food consumption, resource use, food production to calculate use as a per capita nitrogen footprint; it builds on the concept of the carbon footprint; and hence has at least some preprepared public awareness.

Current and predicted Nr 'Creation Rates' (Tg N yr⁻¹) based on population increases alone are given in **Table 1**.

But if it is assumed that everybody in the world has the same nitrogen lifestyle as everyone has currently in the US then the figures in **Table 2** apply.

This year's ECG DGL & Symposium tackled the atmospheric, oceanic and terrestrial impacts that current nitrogen use has on the environment, and was brought to a

formidable conclusion by the Distinguished Guest Lecturer. Briefly, and one hopes not simplistically, the conclusion from all four talks was that a solution to the environmental issues raised by a century's application of the Haber-Bosch process is to reduce consumption.

19

Dr LEO SALTER

Cornwall College, Pool,

Redruth, Cornwall

March 2011

Web link:

The PowerPoint slides from the 2011 DGL and accompanying symposium may be seen on the RSC ECG web pages at http:// www.rsc.org/Membership/ Networking/InterestGroups/ Environmental/ DistinguishedGuestLecture.asp

	Europe	US	S. America	Africa	Asia
1995	32	32	10	5	60
2050	27	42	17	13	92

Table 1: Creation rates based on population increases alone. (Tg N yr⁻¹)

	Europe	US	S. America	Africa	Asia
1995	67	42	87	190	568

Table 2 : Creation rates based on assumption that everyone has current US lifestyle. (Tg N yr^{-1})

Forthcoming Symposium

Environmental Chemistry: A Historical Perspective

A meeting organised by the Royal Society of Chemistry's Environmental Chemistry Group and Historical Group

VENUE: The Royal Society of Chemistry, Chemistry Centre, Burlington House, Piccadilly, London

DATE: Wednesday 26th October 2011

Programme

11:00 am — 11:25 am	Registration, tea & coffee	
11:30 am — 11:35 am	Chairman's introductory comments	Prof. Michael Pilling, Emeritus Professor, Uni- versity of Leeds
11:35 noon – 12:30 pm	Anthropogenic CO_2 and climate change – a historical perspective	Prof. Simon Tett, Univer- sity of Edinburgh
12:30 pm—1:00 pm	'Held fast in the iron grip of frost': Field and laboratory in John Tyndall's dis- covery of the Greenhouse Effect	Prof. Frank James, The Royal Institution
LUNCH: Council Room + Historical Group AGM		
2:15 pm — 3:00 pm	The life and work of Arie Jan Haagen- Smit	Prof. Peter Brimble- combe, UEA
3:05 pm — 3:50 pm	Robert Angus Smith and the search for wider and tighter pollution	Peter Reed, Leominster, Herefordshire
3:55 pm — 4:10 pm	Tea & coffee	
4:10 pm — 4:50 pm	The life and work of Frederick Chal- lenger	Prof. Richard Bushby, University of Leeds
4: 55 pm – 5:35 pm	The emergence of health concerns of the heavy metals and metalloids	Chris Cooksey, London
5:40 – 5:45 pm	Closing comments	

The impact of man on his environment is a major concern for this part of the 21st century. Who were the people who first raised these concerns? What are the key observations behind the debate on climate change? How did experiments with bread crumbs give us an understanding of the environmental chemistry of metals and metalloids? This joint RSC Historical Group and Environmental Chemistry Group symposium will answer these questions and much more. Chemistry provided the medicines, agrochemicals, hydrocarbon fuels, and synthetic materials which propelled the changes of the 20th century. Equally, our understanding of the complex cycles of terrestrial, marine, and atmospheric environments owes much to the ability of chemistry to identify and measure environmental change. Some of the scientists whose work pioneered the discipline of environmental chemistry will be celebrated at this one-day meeting. (See p 21 for an abstract of Prof. Tett's presentation).

REGISTRATION

I wish to attend the RSCHG-ECG Meeting "Environmental Chemistry: A Historical Perspective" and I enclose a cheque for £10.

Admission is by ticket only, for which there is a charge of £10.00. This includes morning and afternoon tea or coffee and a buffet luncheon. To register, please e-mail Rupert Purchase: rp@rupertpurchase.demon.co.uk, and send a cheque for £10.00, **using the form above**, payable to '**RSC Environmental Chemistry Group**' to: Miss Jo Barnes, Hon. Treasurer ECG, Room 3Q11, Faculty of Environment and Technology, University of the West of England, Coldharbour Lane, Bristol BS16 1QY.

Any queries from RSCHG members please contact Bill Griffith, w.griffith@ic.ac.uk

Anthropogenic CO₂ and climate change – a historical perspective

Dr Simon Tett, University of Edinburgh

ABSTRACT: The Climate is what we expect; weather is what we get. Thus, climate change is change in the type of weather we expect. Observations of weather began in Europe in the late 17th century and spread to most parts of the world by the 1950's. By the late 1930's Callendar had compiled weather records and claimed that the Earth was warming. 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 to 2010 while uncertain proxy records of the last millennium suggest that the 20th century warming is unprecedented

The first direct measurements of carbon dioxide in the atmosphere were taken in Keeling at Mona Loa, Hawaii in March 1958 and have been sustained, despite the foolishness of funding bodies, to this day. Annual average CO2 concentrations increased from 316 ppm in 1959 to 390 ppm in 2010. Levels of other greenhouse gases such as methane, nitrous oxide and the chlorofluorocarbons have also increased. Tiny bubbles of air are captured in the Greenland and Antarctica ice-caps as they are formed, and the contents of these air bubbles can be analysed to tell us how atmospheric concentrations of greenhouse gases have changed over the last 800,000 years. Apparent in these records are the great swings associated with extensive northern hemisphere glaciations. At times of peak glaciation atmospheric CO₂ levels are about 180 ppm, while in inter-glacial periods they reach values of about 280 ppm. Current atmospheric CO₂, and other greenhouse gas, concentrations are unprecedented in this record.

Writing in the early 19th century, Fourier suggested that the Earth was warmer than would be expected given radiation from the Sun. By the 1850's Tyndall had shown that water vapour and other gases absorbed infra-red radiation and were largely transparent to incoming solar radiation. In the late 19th Century Arrenhius proposed that CO_2 and other gases through their absorption of infra-red radiation caused the surface warming and calculated how changes in CO_2 might warm the Earth's surface.

The development of models of the atmosphere in the 1940s-1950s led to the general circulation models in use today. These models simulate the atmospheric, oceanic and land surface flow on a grid of O(100x100) km. Using these models, scientists have managed to simulate the 20th century and make projections of future climate change in response to possible future changes in the atmospheric concentration of carbon dioxide and other greenhouse gases.

Biographical details

Simon Tett is Chair of Earth System Dynamics at the University of Edinburgh where he has been since 2007. His current areas of research are understanding the causes of historical climate change and using current climate and change to constrain future climate change. Before that he was Managing Scientist at the Met Office's Hadley Centre leading a team building climate records for the instrumental period. From 1991-2000 he was a scientist at the Hadley Centre working in "detection and attribution" of climate change. His proudest moment was the first, and surprisingly successful, attempt to simulate the 20th century with a general circulation model. He has published more than 50 papers on climate variability and change in both models and reality.

ESED Interest Groups

The recent restructuring of the RSC has led to the creation of the Environment, Sustainability and Energy Division (ESED). The ECG is one of the five component interest groups of ESED, as **Brian Carter** from the Royal Society of Chemistry explains.

Environmental Chemistry Group

The Environmental Chemistry Group (ECG) covers all aspects of chemical behaviour in the environment. The interests of the group include chemical species in water, soil, rock and atmospheric environments, exploring their sources, reactions, transport and fates, and in particular their effects upon each of these environments. Chemicals may be of natural, anthropogenic, biogenic or geochemical origin.

The group aims to promote the interests and expertise of its members, to facilitate scientific discussion relating to environmental chemistry, and to provide expert advice both within the RSC and externally. The group is affiliated to the RSC's Environment, Sustainability and Energy Division, and is actively involved with the sub-group that oversees RSC's membership of the UK Chemical Stakeholder Forum, a Defra body (Department for Environment, Food and Rural Affairs) that advises Ministers.

Regular activities include publication of the biannual ECG *Bulletin*, which is provided to all members, and the annual Distinguished Guest Lecture (DGL) & Symposium, at which a number of invited speakers address a specific topic for a general audience, in support of the DGL award to an eminent figure in the field. Recent DGL topics include: The Future of Water, The Science of Carbon Trading, Environmental Chemistry in the Polar Regions, and in 2010, 'King Coal': Future Prospects for Growth, Use and Clean Technologies. The group also organises meetings of more specialist interest, such as a Contaminated Land event and the Atmospheric Chemistry Forum for early career researchers.

For more information on the activities of the Environmental Chemistry Group, please see

http://www.rsc.org/Membership/ Networking/InterestGroups/ESEF/

For general enquiries, please contact: Brian Carter.

Toxicology Group

The RSC **Toxicology Group** exists to represent and inform members in the RSC of matters pertaining to the risks from chemicals in the work place and in the environment. This is distinct from the issue of environmental contamination as the group seeks to address the toxicological implications and risk management of chemicals.

Since the Group members have an immense amount of experience, the RSC Toxicology Group has an important input into the Environmental Health and Safety Committee (EHSC) of the RSC, which is the main policy unit on health, safety and environmental issues. Thus the RSC Toxicology Group has a significant voice in the RSC and its public advice service. The recent major restructuring of the RSC activities in the health, safety, environmental, energy, and related areas to form a new body entitled the 'Environment, Sustainability and Energy Division' (ESED) is very pertinent to the areas of expertise of the RSC Toxicology Group and will ensure its important role in RSC business.

The RSC Toxicology Group maintains formal links with the British Toxicological Society and the Royal College of Pathologists. Members of the group and Committee come from academic, public and commercial enterprises. Every effort is made to encompass all shades of experience. Occasional scientific meetings are arranged on topics considered to be of interest to the members and others in associated fields.

Water Science Forum

The Water Science Forum (WSF) is one of the most active of the Royal Society of Chemistry's (RSC) Subject Groups. It focuses on the application of chemical sciences in the management of the water cycle and the impact of these activities on the natural environment. WSF attracts members, and thus expertise, from many sectors within the water community: environmental consultancies, utility companies, industrial treatment companies, academia and regulatory bodies.

The broad aim of the WSF is to promote the professional and scientific interests of members and to advise on and influence, in the public interest, the application of Environmental chemistry in water-related industries.

WSF key OBJECTIVES are:

- To keep members up-to-date with current developments within the water sector and to promote Continuous **Professional Development**
- To provide a forum for the • debate of professional and scientific matters on waterrelated issues within the RSC and other relevant organisations
- To provide specialist technical advice on waterrelated issues to the RSC and to assist the RSC in presenting a corporate view to national and local government on matter of interest to WSF members
- To promote research, education and specialised training in all aspects of water-related chemistry, including relevant chartered status for members.

The WSF achieves this by:

- Organising topical meetings and conferences
- Providing financial assistance to encourage professional development
- Contributing to consultation documents from the UK and EC.

International **Network of Forensics**

The International Network of **Environmental Forensics (INEF)** was founded in 2008 for the express purpose of providing a forum for scientists, environmental consultants, regulators and attorneys to share information regarding the use of environmental forensics. Environmental forensics is the use of scientific techniques to identify the source, age and timing of a contaminant into the environment.

INEF is involved with the design and delivery of a number of outreach programs, including conferences and workshops, to interested parties throughout the world. Information shared through these outreach programs provide investigators employing environmental forensic techniques with the most current scientific information available to identify the source, age and timing of contaminant release to the environment.

Energy Sector

The mission of the Energy Sector is to provide a forum for members of the Sector, Division, RSC and others to access knowledge and express views on chemical, legislative, educational and other matters relating to energy and to promote the interests, both within the RSC and externally, of the members of the Sector and the Division.

The responsibilities of the Energy Sector are:

To support the professional interests of members of the Sector, the Division and the RSC

- To organise scientific meetings and, where appropriate, to publish proceedings
- To provide information and advice to educators and others
 - To interact with and to encourage interaction between other RSC groups and external professional bodies
 - To assist in the promotion of links between academic and research organisations and energy related industries
- To act as the focal point for well-based, critical and knowledgeable discussion on the chemistry involved in energy related science and industry

.

•

- To assist the Division in its public relations activities in matters concerning energy and to help promote public awareness of the important role that chemistry plays in the production, utilisation and dissipation of energy
- To assist the Division in its work with government and its agencies and provide input, as a recognised consultative body, to the RSC's position papers which respond to any actions that may affect the interests of the Sector.

BRIAN CARTER

Programme Manager, **Environmental Sciences** Royal Society of Chemistry, Thomas Graham House, Cambridge CB4 0WF Tel: 01223 432424

Recent books on the environment and on toxicology at the RSC library

The following books on environmental topics and toxicology have been acquired by the Royal Society of Chemistry library, Burlington House, during the period July 2010 to June 2011.

N. G. Halford, Royal Society of

Chemistry, Cambridge, 2011, Shelf

Pollution and Heart Disease

Environmental Cardiology:

A. Bhatnagar, Royal Society of Chemistry, Cambridge, 2011, Shelf Mark: 628.52:616

Micro-facts: The Working Companion for Food Microbiologists

P. Wareing, Royal Society of Chemistry, Cambridge, 2010, Shelf Mark: 579

Website: RSC eBook

Silver in Healthcare: Its Antimicrobial Efficacy and Safety in Use

A. B. G. Lansdown, Royal Society of Chemistry, Cambridge, 2010, Shelf Mark: 615.9

Website: RSC eBook

A new online facility now allows RSC members to search the library catalogues and save their searches. Go to http://www.rsc.org/opac for

Aspects of African Biodiversity

Proceedings of the Pan Africa Chemistry Network Biodiversity Conference, Nairobi, 10-12, September 2008

Royal Society of Chemistry, Cambridge, 2009

Editors: Jacob Midiwo and John Clough ISBN: 978-1-84755-948-7 Price: £99.95

Synopsis

Energy Crops

Mark: 662:628.5

This book is the proceedings of the Pan Africa Chemistry Network Biodiversity Conference which was held in September 2008. A key aim of the RSC/Syngenta Pan Africa Chemistry Network (PACN) is to connect African scientists through a cycle of conferences and workshops and this conference held at the University of Nairobi was the first of these. It brought together 26 speakers from nine African countries – Kenya, Ethiopia, Tanzania, South Africa, Nigeria, Botswana, Uganda, Zimbabwe and Sudan – plus the UK and Brazil. The lectures covered topics such as making the best use of the diversity of Africa's plants in agriculture and medicine whilst benefiting communities in Africa; natural products; analysis and the environment; water quality; dealing with waste; biofuels; understanding crop protection chemicals in the African context; agricultural practices for Africa; farm animals; conservation and the impact of tourism on biodiversity. The resulting book provides a valuable overview of several aspects of biodiversity in Africa.

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, 1 Eastern Road, Haywards Heath, West Sussex RH16 3NG Tel: 01444 456673.