THE ROYAL SOCIETY OF CHEMISTRY
ENVIRONMENTAL CHEMISTRY GROUP

Bulletin

January 2006

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Wheal Coates, one of many redundant tin mines in Cornwall, and a potential source of airborne arsenic. Monitoring of air particulate arsenic levels in Cornwall: p 17

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(from March 2005)

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Arsenic in the air

Munir Thalib's attempt to find sanctity in the Netherlands failed. Two hours from Schiphol airport in September 2004 on a flight from Jakarta, Indonesia's leading human rights activist died. A post-mortem examination revealed 465 milligrams of arsenic in his stomach and 3.1 mg and 4.6 mg of the same substance in his blood and urine, respectively. The conclusion of the trial of the alleged lone suspect for this murder in December 2005 left more questions than answers. But the choice of arsenic as the murder weapon highlighted the continuing fascination for this poison.

Away from day-to-day headlines, the struggle to cope with the arsenic contamination of drinking water in Bangladesh and elsewhere interweaves environmental and analytical chemistry with political goodwill. In this issue of the *ECG Bulletin*, we return to this story with contributions from many of the UK scientists who are active in unravelling arsenic's legacy. Two UNICEF workers, **Rick Johnston** and **Ross Nickson** report on the current situation in Bangladesh and northern India, respectively. The uptake of arsenic by paddy rice is a particular concern of **Andy Meharg**, while another University of Aberdeen scientist, **Jörg Feldmann**, uses coupled mass spectrometric techniques in his quest for understanding arsenic speciation. **Chris Harrington** and co-workers from De Montfort University show how dried hyacinth roots may be a potential method for removing arsenic from contaminated groundwater. Concerns about exposure to arsenic have reached outside Asia. In Cornwall, soil is contaminated with arsenic from past industrial activity. The **Air Quality Unit** at **Cornwall College** has checked if this contaminated soil has resulted in measurable levels of particulate arsenic in the air in west Cornwall.

In the January 1999 issue of the *ECG Newsletter*, we reproduced the note from *Nature* (1998, **395**, 338), which explained the geochemical conditions for the presence of elevated arsenic levels in the Ganges aquifers of Bangladesh. We are now pleased to publish a background article on arsenic pollution of groundwater in Bangladesh by one of the authors of that note, **John McArthur**. This article appears on the *ECG Bulletins* section of the RSC homepage.

Arsenic contamination of drinking water in Bangladesh and northern India: an update

From a distance, and through a myriad of conference reports, papers in the primary literature, and the occasional mention on the main news channels, it is difficult to gain an impression of what is actually happening to solve the arsenic crisis in Asia. We are therefore grateful that two UNICEF Officers who work in two of the affected regions, **Rick Johnston** and **Ross Nickson**, agreed to respond to some questions on the current situation.

Bangladesh

Exposure: How many provinces in Bangladesh have been affected? Approximately how many people in these areas have been exposed to arsenic in their drinking water? What percentage of the population in Bangladesh has been affected?

Over the past five years, Bangladesh has conducted one of the largest water quality screenings ever made. On the basis of national random surveys made in the late 1990s by the British Geological Survey and by the Department of Public Health Engineering with UNICEF support, 270 upazilas (sub-districts) suspected to be 'arsenic-prone' were identified and selected for blanket screening: testing of every single well. The bulk of the testing took place between 2000 and 2003, but some screening work has continued into 2005. Over five million wells have been tested to date, which is equivalent to making over 3,000 tests per day, every day, for over four years. During the field testing, testers provided information about arsenic to tubewell owners, and painted the wells after getting test results – red for wells above the permissible limit of 50 parts per billion (ppb) and green for wells within the limit. Of the 4.8 million wells so far entered in the national database, 1.4 million (30%) were found to be contaminated.

The testing results are most useful at the village level as they allow villagers to know which wells should be used for drinking and cooking, and which ones should be used only for washing and other domestic purposes. The dataset is also tremendously valuable for making regional analysis of contamination at different scales, from village to national. It is not helpful to consider entire political units as 'arsenic-affected' if a very small number of wells are contaminated. For instance, in Dinajpur District, 32,194 wells were screened, and only 62 found contaminated. This is less than 0.2% contamination, and the district as a whole should be considered unaffected by arsenic.

More usefully, areas can be categorized into different levels of risk based on the proportion of tubewells that are contaminated, as shown in Table 1. It should be remembered that at the local level it is the arsenic concentration in individual wells, rather than the proportion above 50 ppb, which determines risk: a red well containing 600 ppb is roughly ten times as dangerous as a red well containing 60 ppb. There are 'hot-spots' in largely uncontaminated districts and upazilas where a few wells have very high levels of arsenic, even above 1000 ppb. However, in general the highest concentrations are found in the areas where the highest proportions of tubewells exceed the drinking water standard.

The government *Implementation Plan for Arsenic Mitigation* calls for

Table 1: *Proportion of wells exceeding 50 ppb standard at different scales*

Proportion of Wells > 50 ppb	*Districts*	*Upazilas*	*Unions*	*Villages*	*Population* (millions)*
<= 5%	7	35	668	22,544	22.3
>5-40%	31	145	1,176	14,788	20.8
>40-80%	15	65	621	8,331	11.7
>80-100%	1	23	416	8,378	10.1
Total affected	47	233	2,213	31,497	
Total screened	54	268	2,881	54,041	64.9
Total not screened (likely unaffected)	10	204	1,603	33,278	75.1
Total in country	64	472	4,484	87,319	140†

*Sum of village population by risk category
†Approximate – exact number not known

Table 1 shows that 47 districts, 233 upazilas, 2,213 unions, and 31,497 villages can be considered 'arsenic-affected' – that is, more than 5% of wells in these areas exceed the permissible limit. In 2,316 villages, home to 1.2 million people, every single well tested was found contaminated.

'emergency response' in villages having more than 80% of wells contaminated. Villages having high numbers of patients or pockets of high arsenic concentrations can also be classified as 'emergency villages'. Villages with 40-80% contamination are considered for a medium-term response, while villages with lower levels of contamination would be addressed in the long term.

In all of the grossly contaminated areas, blanket screening has now been completed. While there are undoubtedly some arsenic-contaminated wells in the upazilas which were not covered with blanket screening, national surveys suggest that contamination in these areas will be small – less than 2% on average. Thus the proportion of tubewells affected at the national level is much less than 30%. Based on our best estimates of tubewell density in the unscreened upazilas, we calculate that there are approximately 8.6 million tubewells in the country, giving a national contamination rate of approximately 16%.

During blanket screening, a population count of each village screened was made. In total, nearly 65 million people, just under half of the estimated population of Bangladesh, reportedly live in villages which were screened. Table 1 shows the village population by different risk categories. By multiplying the proportion of contaminated wells at each village by the village population, we calculate that 20.2 million people – about 14% of the total national population – are at risk of arsenic exposure. (An alternate way to calculate the population at risk is to sum the number of reported users per red tubewell. This approach gives an estimate of 19.4 million people).

However, the proportion of contaminated wells in a village is different from the proportion of people drinking contaminated water in a village. Because of the national information campaign, and the policy of blanket testing and painting of tubewells, families with red tubewells can and do choose to collect drinking water from safe sources. Surveys which measure arsenic in drinking water at the household level, as opposed to at the tubewell, routinely find lower contamination rates. The Bangladesh Demographic and Health Survey (BDHS, 2004) found only 9% of households nationwide had drinking water in the house containing more than 50 ppb arsenic. So the population actually drinking arsenic-contaminated water in the home is most likely in the range of 10-15 million.

Bhanga upazila. Bhanga upazila in Faridpur district is heavily arsenic-contaminated: blanket testing determined that 91% of wells exceeded 50 ppb. In the British Geological Survey's 1999 national survey, the average concentration of arsenic in Bhanga tubewells was nearly 250 ppb. However, a 2005 field survey found that in 52% of households having a red tubewell, arsenic levels in household drinking water met the drinking water standard. Villagers reported that they travelled significant distances to collect drinking water from safe sources, primarily newly installed deep tubewells.

Geochemistry: What concentration range of arsenic has been found in drinking water?

Commonly <5 to 500 micrograms per litre. See Figure 1, which is based on data from DPHE/MML/BGS (1999) and DPHE/BGS/MML (2001)

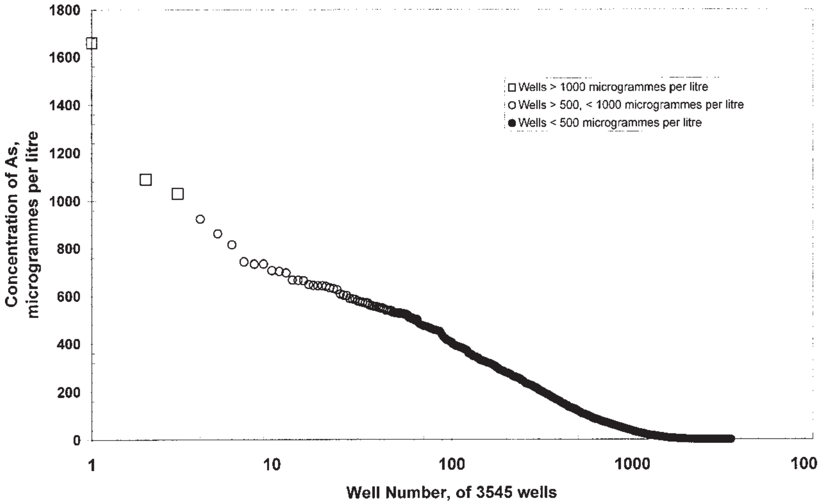

Figure 1: *Range of arsenic levels ($\mu g\ L^{-1}$) in well water*

Data from: DPHE/MML/BGS. 1999. Groundwater Studies for Arsenic Contamination in Bangladesh. Rapid Investigation Phase. Final Report. Mott MacDonald Ltd and British Geological Survey. Report prepared for Department of Public Health Engineering (Bangladesh) and Department for International Development (UK).
DPHE/BGS/MML. 2001. Arsenic contamination of groundwater in Bangladesh. Department of Public Health Engineering and British Geological Survey. BGS Technical Report WC/00/19 (4 vols).

Are the underlying geological reasons for the presence of arsenic in wells used to supply drinking water, the same?

The reason is the same the world over, except for rare instances. The reason is reductive dissolution of iron oxides, which sorb arsenic strongly, and so release it when dissolved. The exceptions are (1) locally in Michigan, where local wells intercept sulfide mineralization at shallow depth and allow oxidation; (2) locally near Perth, where dewatering of sulfidic peat leads to oxidation, acidification, and arsenic release, and (3) in the interior of Argentina, where dissolution of volcanic glass gives arsenical water in shallow wells.

Health Effects: What symptoms of arsenic exposure are being observed? Is the monitoring of arsenic exposure in affected populations adequate? Are arsenic-related incidences of cancer increasing?

In conjunction with the massive tubewell screening campaign, an arsenicosis patient identification campaign was carried out. In some areas house-to-house visits were made, while in others ‘arsenic camps’ were held where suspected cases could be identified. The skin lesions characteristic of arsenicosis were the primary diagnosis tools, with melanosis (changes in skin pigmentation) and keratosis (hardening of the skin on palms and soles) as the most commonly identified conditions. To date 37,749 cases have been identified through patient surveys. However, there are some problems with the available health data and it is not clear whether this is an accurate figure.

Government doctors and health workers in arsenic-prone upazilas have been trained in identification and management of arsenicosis, and arsenicosis is now a reportable disease, included in the government’s medical management information system.

More serious health effects expected include skin, lung and bladder cancer cases. In particular, lung cancer is expected to cause a significant number of deaths in the future. While some cases of cancer have been identified among arsenicosis patients, and some deaths have undoubtedly occurred, reliable numbers are not available.

Remediation: How effective is the national and international effort to prevent arsenic exposure? What international agencies are involved? What techniques and strategies are being used to remove arsenic from drinking water or to prevent exposure to arsenic?

The focus of arsenic mitigation efforts in the first few years of the decade was on blanket screening and raising awareness, but as those activities were gradually completed the emphasis shifted towards provision of safe water options in affected areas. The government *Implementation Plan for Arsenic Mitigation* (2004) calls for giving top priority to ‘emergency villages’ – those having at least 80% of tubewells contaminated, or having a significant number of arsenicosis patients. Villages having from 40-80% contamination are to be targeted for intervention in the medium term, while villages having less than 40% contamination can be addressed as part of a long term rural water supply strategy.

A number of organizations have provided arsenic mitigation options in affected areas. The two largest projects specifically designed for arsenic mitigation are those of DPHE/UNICEF and the World Bank/SIDA-funded Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP). A number of NGOs, notably World Vision International, NGO Forum for Drinking Water and Sanitation, and IDE have also supported installation of sizable numbers of safe water options. Two large government water and sanitation programmes (GOB-IV and DPHE/DANIDA) have installed many water options in arsenic-affected areas, though these programmes are not specifically designed for arsenic mitigation.

In the 270 upazilas considered arsenic-prone, the arsenic mitigation projects have installed approximately 21,000 safe water options in the last five years. The GOB-IV and DPHE/DANIDA projects are much larger, and have installed over 85,000 safe water options in these upazilas. Taken together, these roughly 107,000 water options have the capacity to provide safe water to about 4.5 million households, or 38% of the total population in the arsenic-affected areas. Many of these 107,000 water options are likely serving people who are not currently exposed to arsenic. Table 1 shows that over 40% of villages in the arsenic-prone upazilas have less than 5% arsenic contamination, and only about 16% of villages would be considered for the ‘emergency phase’. The GOB-IV and DPHE/DANIDA projects, which are not expressly designed for arsenic mitigation, certainly have allocated many water points to non-affected areas. Unfortunately, not all of the datasets provide allocation information to the village level so it is not possible to clearly assess the current situation in the 8,378 villages with at least 80% contamination. In particular, the large GOB-IV dataset has only limited disaggregation.

Looking at the DPHE/DANIDA and arsenic mitigation projects for which village-level locations are available, 12,168 alternative water supplies have been installed in 2,133 emergency villages (25% of the total). These water points have the capacity to provide water to 350,000 households, or 86% of the population of these villages.

More data is available disaggregated to the union level; in the 416 unions where 80% or more of tubewells are contaminated, at least 17,540 safe water options have been installed, which can serve 1.3 million households, or 47% of the population of these unions. At least another 27,779 alternative water sources have been installed in unions having 40-80% contamination. These are sufficient to supply about 425,000 households, or 30% of the total population in these unions. A further 34,000 water options have been installed in unions with <40% contamination, mostly through the GOB-IV project. These could provide safe water to a further 650,000 households, or about 10% of the population in these unions.

Deep tubewells have been the principal water supplies installed in arsenic-affected upazilas, primarily through the GOB-IV and DPHE/DANIDA projects. These account for 70% of all alternate water supplies in these areas. Domestic rainwater harvesting units have been the next most commonly installed units, followed by dug wells, shallow shrouded tubewells, arsenic/iron removal plants, and pond sand filters. A limited number of other technologies such as rural piped water supplies and arsenic removal filters (both community and household level) have also been installed.

Future: What are the hopes for the next five years?

Many of the arsenic mitigation projects are nearing completion in 2005, including BAMWSP and DPHE/UNICEF. The current phase of the DPHE/DANIDA project is also nearly finished. The World Bank is supporting a new project, the Bangladesh Water Supply Programme Project (BWSPP) which will have a significant arsenic mitigation component, focused on rural piped water supply. Both DPHE/UNICEF and DPHE/DANIDA are currently designing water and sanitation projects which will run for the next five years and include significant arsenic mitigation activities. BRAC is seeking funding for a water and sanitation project which could provide some arsenic mitigation activities. The new DPHE/UNICEF project will cover approximately 4,000 emergency villages, and other projects will cover an additional 1,200 emergency villages. A regional analysis indicates that virtually all of the emergency phase villages should be covered by one mitigation project or another over the next five years.

The majority of villages in the arsenic-prone upazilas have under 80% contamination, and is expected that the major water supply projects will contribute significantly to reducing arsenic exposure in these villages as well.

Northern India

Exposure: How many provinces have been affected?

Naturally occurring arsenic in alluvial aquifers: West Bengal, Assam, Bihar, Uttar Pradesh (UP), Jharkhand in predicted order of severity of problem. There is a likelihood that arsenic will also be found in Tripura in the North-East. Arsenic also reported in very localised areas in Chattisgarh state. This seems to be related to hydrothermal enrichment.

Approximately how many people in these areas have been exposed to arsenic in their drinking water?

No accurate estimates. A Government of West Bengal publication suggests 13.8 million people may be ‘at risk’ in that State. This means living in an area known to be arsenic affected. Some more accurate estimates for West Bengal should be available once arsenic test data of all government handpumps is collated and mapped, which is currently ongoing. Jadavpur University in Kolkata states in a recent CD-ROM presentation that 9 million are expected to be drinking water with >10 μg/l and 7 million expected to be drinking water with >50 μg/l. They expect 300,000 people will be arsenic affected (this is based on those expected to be drinking > 300 μg/l).

So far in two districts of UP (Lakhimpur Kheri and Ballia) where screening testing is complete 2% and 4.4% of sources have > 50 μg/l respectively. A simple calculation based on the populations of the districts gives around 65,000 and 120,000 people whose sources are affected respectively. 49 further districts have been identified for priority testing out of a total of 70 districts in the state. Overall I expect it will be found that < 2 % of sources in UP are arsenic-affected but with a population of around 170 million that still amounts to several million people at risk.

In Bihar and Assam the % of sources contaminated and corresponding numbers of people affected will be somewhere between UP and West Bengal. If you put all of these figures together I think you can confidently say that at the current time in India > 10 million people are regularly drinking water with > 50 μg/l of arsenic.

Health Effects: What symptoms of arsenic exposure are being observed?

Initial symptoms are similar across the region: melanosis (changes in skin pigmentation) and keratosis (hardening of skin on palms of hands and soles of feet). This may lead to skin cancers and other problems. I have seen people showing these symptoms in West Bengal, Bihar and Uttar Pradesh. Other effects are being reported such as respiratory problems and persistent coughing. Internal cancers of the lung, bladder and liver are later stage complications.

Is the monitoring of arsenic exposure in affected populations adequate?

In West Bengal the systems are now largely in place. A network of district laboratories has been established and all government handpumps have been tested. ‘Arsenic clinics’ are underway at block and district level and potential arsenicosis patients are being screened, diagnosed, reported and treated. In other states development of awareness about the problem and development of institutions to test for arsenic, identify patients etc is still underway but progressing.

In UP the UP Jal Nigam (the relevant govt. department) with UNICEF assistance are screening for arsenic in selected blocks in 51 out of 70 districts using field test kits. A total of about 100,000 sources will be tested. This will give an initial picture of which parts of the state are affected.

Are arsenic-related incidences of cancer increasing?

Undoubtedly, although accurate data linking the two is often not available. Only recently has ‘arsenicosis’ been recognised as a reportable disease in West Bengal and the system for reporting cases is now being strengthened. The problem of misdiagnosis where the effects of arsenic are ascribed to something else is certain to be there in areas where arsenic is not yet well known about by the health system.

Remediation: How effective is the national and international effort to prevent arsenic exposure?

In West Bengal the programs are well advanced. The scale of the problem is well defined and schemes to address it are underway including provision of piped treated surface water, drilling of deeper wells and provision of domestic and community-based filter systems. That said there is still much more to be done. Convincing people to switch to an alternative water source or treat their water is difficult. The alternatives are almost always less convenient and require more effort than their existing handpumps. And as people have more immediate and pressing problems, unless they physically see the effects of arsenic on themselves or others, they are reluctant to change their habits. As the majority of handpumps are privately owned, it is not possible to force them to change their habits by removing the unsafe source.

In other states the magnitude of the problem is still being uncovered by screening testing. Where it is known about, small scale efforts have been made to promote well-switching (using arsenic-safe handpumps) and provide alternative sources. In some states steps have been taken to close arsenic-affected handpumps where that is possible. When the screening gives the true magnitude of the problem and the affected areas are identified the next step will be focus on preventing arsenic exposure in these areas.

What international agencies are involved?

UNICEF, WHO, DFID, World Bank in India.

What techniques and strategies are being used to remove arsenic from drinking water or to prevent exposure to arsenic?

Various methods based either on *source substitution* or *arsenic removal*:

Source substitution:
- Piped water schemes using either treated surface water or deep groundwater.
- Deep boreholes fitted with handpumps.
- Rooftop rainwater harvesting schemes.
- Use of shallow groundwater from protected, cleaned, sterilised large-diameter dug wells

Arsenic removal:
- Domestic point-of-use filter systems.
- Community-based handpump-attached filter systems.
- These are both generally based on techniques which absorb arsenic onto various types of filter media i.e. activated alumina, iron oxides *etc.*

Future: What are the hopes for the next five years?

The overall hope is that exposure of the population to arsenic can be substantially reduced leading to less people contracting arsenic-related diseases in the future. This requires that the affected areas are accurately defined and sustainable alternatives taken up by the community to reduce their intake of arsenic.

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The note on the geochemistry of arsenic in Bangladesh was written by Professor John McArthur, University College, London. http://www.es.ucl.ac.uk/people/mcarthur/

Banglapedia http://banglapedia.search.com.bd/index.html is a useful website for information about the geography and history of Bangladesh and surrounding regions.

Arsenic contamination of paddy rice in Bangladesh

Professor Andy Meharg describes how arsenic contamination affects the basic food of the Bengal Basin, rice, and with his first hand experience of the region, stresses the urgency needed to solve the crisis.

Unintentional (and intentional) misuse of arsenic compounds

The element arsenic is synonymous with poison, and since early history its potent properties have been exploited for good and evil (Meharg, 2005). Arsenic minerals, such as the sulphides realgar (As_4S_4), orpiment (As_2S_3) and arsenopyrite (iron arsenide sulfide), are often associated with precious and base metal ores. The former two caused havoc when they were widely used as a red and yellow pigment respectively. Arsenic trioxide, which is released into the atmosphere and condenses in chimneys on smelting ores of tin, copper and other metals, is the most notorious of all arsenic compound; the soluble, clear and tasteless "inheritance powder" of the French aristocrats. Victorian Britain was poisoned by the green pigments copper arsenite ($CuAs_2O_4$) and cupric acetoarsenite [$Cu_4(OAc)_2(AsO_2)_6$]. The latter was used widely as a wallpaper, food and clothes dye (Paris green; C.I. Pigment Green 21).

Geochemistry of arsenic in Bangladesh and northern India

But arsenic poisoning is not confined to the past, and it was not mankind but nature that so subtly delivered the poison over many decades, which has led to the present tragedy. The source of the disaster, which has unfolded in Asia, was the trace amounts of arsenic found in all rocks, solubilised during erosion as pentavalent arsenate (AsO_4^{3-}) under oxidized conditions, or trivalent arsenite [$As(OH)_3$] under anaerobic conditions.

Sediments that are carried down by the vast network of rivers draining the Himalayas are coated with iron plaque (iron(III) oxyhydroxide [FeO(OH)]). This plaque very effectively removes arsenate from solution, leading to elevated levels in the FeO(OH), although on a gross basis these sediments are not particularly elevated in arsenic with concentrations around 10 ppm. The sediments are deposited onto the most fertile and densely populated regions of the earth, the Bengal and Mekon Deltas. As the sediments are laid down with successive yearly depositions, organic matter buried with them turns their environment anaerobic, dissolving the FeO(OH) due to iron reduction and liberating the arsenic as arsenite.

David Kinniburgh from the British Geological Survey has explained the elevation of arsenic found in the aquifers of these deltas. If 1 ppm of arsenic is dissolved from the FeO(OH), this leads to 6 ppm in groundwater (Meharg, 2005). The highest levels actually observed in the affected regions are never more than 6 ppm, yet 100 fold less arsenic than this in groundwater has severe health consequences if chronically ingested.

Exposure to arsenic from drinking water

Arsenic is an environmental carcinogen and the National Research Council (2001) of the USA calculates that if you drink 50 ppb in drinking water the risk of bladder or lung cancer is around 1 in 100. Over 35 million Bangladeshis alone are drinking this level or higher. Very simple geochemical reactions have lead to vast devastation, the greatest mass poisoning in human history, a catastrophe that is still unfolding.

Over 100 million people, 1.5% of the earth's population, are living on top of these arsenic contaminated aquifers whose waters are tapped through the sinking of tens of millions of tubewells (Meharg, 2005). The wells were sunk in good faith, sponsored by UNICEF and others, to provide drinking water free of the microbial pathogens found in surface waters and shallow hand dug wells, with these pathogens killing a high percentage of young children – around 40% of the under fives. The impact of this tubewell program in Bangladesh, which began in earnest in the 1970s, was to cut child mortality by 50%, a dramatic success. It was not till the late 1990s that it was fully accepted that this microbially clean tubewell water was widely contaminated with arsenic. The poisoned aquifers covered large tracts of the Bengal Delta, centering on southern Bangladesh, with over 50 million people drinking water with above 10 parts per billion (ppb) arsenic (BGS, 2001), the level above which water is considered to be unsafe in the US, West Bengal and Europe.

A public health disaster

High rates of arsenical disease are observed in affected regions including hypo- and hyperpigmentation (white and black rain drop sized marks) of the skin, leading to keratosis (arsenic warts), which develop into skin cancer. Arsenic ingestion also leads to high rates of bladder and lung cancer, as well as premature and aborted births. People with arsenical skin diseases are treated as outcasts, particularly young women who are rejected for marriage, leaving them with little or no social infrastructure to support them through their illness.

Warnings of this impending disaster were published in India as early as 1983, but unfortunately they were ignored (Meharg, 2005). The early providers of the tubewells were oblivious to the geological cycling of arsenic. However, if the groundwater had been properly chemically tested before initiation of the tubewell sinking programs, this crisis would not have occurred.

This public health disaster is marked by staggering inertia by the international aid community. Tubewells became part of the infrastructure of life of SE Asia, with the number of wells sunk doubling in Bangladesh alone during the 1990s (BGS, 2001). Even in 2005 a coherent plan to deal with the crisis has still not been developed, despite the realisation that the scale of the crisis was growing year on year, with more and more arsenic affected aquifers being discovered throughout South East Asia. China, Nepal, Pakistan, Iran, Myanmar, Vietnam, Laos have all be added to the list of affected countries (Meharg, 2005). In the Indian sub-continent where the crisis was once limited to the Bay of Bengal, arsenic affected aquifers have now been found higher up the Ganges and out with the Gangetic plain.

Solutions to the problem

In the worst affected country Bangladesh, over 100 million US dollars have been lent by the World Bank to fight the crisis over an eight year period. This sum is less than a dollar per Bangladeshi – 12.5 cents per person per year. Even spending this small amount has been problematic with the World Bank only wanting the money to be spent on well-thought out solutions to the crisis.

However, practical solutions are thin on the ground. Many mitigation technologies have been developed and tested. But most were found to be inadequate, mainly because they require an infrastructure (roads, distribution, power, routine maintenance, and change in culture) that Bangladesh cannot offer. The Bank has settled on piping clean water from unaffected regions to affected regions, and providing village stand pipes where necessary. Given that there are some 80,000 villages in Bangladesh, this is a monumental task and will cost much more than 100 million dollars.

And where will this clean water come from? As surface waters still carry the microbes that caused so much health devastation, these waters can only be used if water treatment plants are installed, which would have to be of a massive capacity. If unaffected groundwater is to be used, the demand on the aquifers will be substantial, and it is likely that problems will arise due over exploitation. Piped water will also have to cope with the very mobile geography of Bangladesh, with the constant moving of river channels routinely destroying infrastructure.

The best solution is to build and maintain village based surface water based treatment plants, but for this to be successful the infrastructure of Bangladesh needs substantial and rapid upgrading. Who is going to foot the bill? In a country that is flooded once a year and has multitudinous rivers fed by the great Ganges and Bramaputra, shortage of water should not be a problem. Bangladesh's water crisis could be solved if the international will and cash were available.

Testing the drinking water

Most aid money for fighting the arsenic crisis has been channelled into testing tubewells to check if the drinking water is safe. Yet the upper arsenic level set by these tests is too high. The Bangladesh standard is 50 ppb arsenic. Most risk assessors agree that 10 ppb should be the maximum amount of arsenic present in drinking water.

Arsenic in tubewells is generally tested using field kits. But for low levels of arsenic, the colorimetric assays used in these kits are inadequate. Leading arsenic researcher Dipankar Chakraborti, based in Kolkata, found field test kits are unreliable (Meharg, 2005). Tubewells are marked red for above 50 ppb and green for below 50 ppb. But it is well known that levels fluctuate in wells over time, rendering the well marking program inaccurate. There are over 10 million tubewells in Bangladesh. Well testing is slow and cannot cope with the current number of wells, never mind the rapid number of new wells which are still being sunk. Well testing in any case can only be a short-term measure; the aim must be to find alternative drinking water sources for the affected regions.

Arsenic-contaminated rice

But the problems do not stop there. The Green Revolution led to two rice crops per year harvested from most Bangladeshi paddies. This double cropping has enabled Bangladesh to be nearly self sufficient in rice. Unfortunately, dry season rice production is dependent on groundwater irrigation, and in the south of Bangladesh this irrigation water, like the drinking water, is tainted with arsenic.

My research, and others, has shown that arsenic is accumulating in paddy soils. This has resulted in elevated arsenic in rice grain (Meharg and Rahman, 2003). Average dry season arsenic levels in rice grain for the south of Bangladesh are so high – around 0.3 ppm – that a person eating a subsistence rice diet of 0.42 kg rice per day is consuming the equivalent amount of arsenic present in 3L of 50 ppb arsenic-contaminated drinking water. So people in affected regions who are drink 50 ppb arsenic in their water are actually exposed to double the quantity of arsenic. Dietary exposure to arsenic through rice consumption must therefore be recognised as a factor in this crisis.

The chemistry of arsenic is responsible for elevated arsenic levels in rice grain. Rice has the highest levels of arsenic in grain of any cultivated grass, even in "uncontaminated environments". This is because paddy soils are anaerobic while other grain crops are grown on aerobic soils. Under anaerobic conditions, arsenate is reduced to arsenite. Arsenite is much more mobile in soil solution than arsenate because it is uncharged at the relevant pHs of soil (i.e. it is present as undissociated arsenious acid, H_3AsO_3, pK_a 9.2). Arsenite is readily accumulated by rice roots, surprisingly entering into the roots *via* water channels (aquaporins). This uptake is facilitated by arsenite's uncharged state and relatively small size (Meharg and Jardine, 2003).

Crop irrigation and politics

The food issue should not be overlooked. If clean drinking water is provided tomorrow, the paddy fields will still have been irreparably contaminated. Cleaning up arsenic from drinking water is difficult enough, never mind tackling the vast quantities of water needed for dry season rice irrigation. It is not an option to stop dry season rice production. Unless alternative irrigation water supplies are found to groundwater, each dry season will see the paddy arsenic levels across Bangladesh increase. The rice problem will get much worse over time. The only adequate way to tackle dry season rice irrigation is to use surface waters in the affected southern regions. The use of what should be bountiful surface water supplies is negated by the retention of a considerable quantity of Ganges water into India at the Bangladesh-Indian border, the main source of political conflict between these two neighbours.

I have travelled around the south west of Bangladesh during the dry season and have seen storage pond after storage pond, canal after canal, dug to supply year round agricultural water, lying dry. Effective and international co-ordination of surface water resources would greatly benefit Bangladesh.

Tackling the crisis

What is needed in Bangladesh and the other arsenic affected regions of SE Asia is decisive and rapid action. The scale and nature of the problem has been characterised, in the worst affected region, Bangladesh and West Bengal, for at least six years. Yet the provision of an infrastructure to give the people of the Bengal Delta the most basic and essential of commodities – safe drinking water – has hardly started.

The aid agencies inadvertently, and with the best of intentions, created the problem by sinking tubewells into unsafe aquifers – without adequately characterizing the aquifers to check the absence of contaminants such as arsenic. We can not literally expose the peoples of the Bengal Delta to a problem that is not of their making. If the aquifers had been characterized properly in the early 1970s before the start of the tubewell programme, then I am certain that technologies and infrastructure would have been deployed to ensure that potential surface water supplies were safe to drink. Now we know the terrible legacy of the tubewell programme, every effort must be made to provide safe drinking and irrigation waters for this region.

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Arsenic speciation in the environment

Introduction

Arsenic is the classic metaphor of a poison popularised in fiction for its lethal properties. But in recent years arsenic has made headlines for its occurrence in well water in parts of Bangladesh, India and Vietnam. Relative small concentrations – up to a few mg/L – in contaminated food and drinking water are not high enough to cause acute signs of arsenic toxicity in humans. However, the effects of prolonged ingestion of sub-acute toxic levels of arsenic become apparent after several years or even decades of exposure. Symptoms of low level arsenic exposure include arsenicosis and hyperpigmentation of the skin, leading to external and internal cancers.

Arsenic in food

The WHO, EU and US-EPA have campaigned to lower the threshold for arsenic in drinking water from 0.05 to 0.01 mg As/L. But there is increasing evidence that arsenic in food also contributes significantly to the overall arsenic burden. In contrast to drinking water, no threshold level for arsenic in food has been established – although some non-legal guidelines exist (1 mg arsenic/kg). The difficulty in establishing a threshold value is due to the range of toxicities of different arsenic species present in food.

Inorganic arsenic, for example arsenite As(OH)$_3$ and arsenate AsO(OH)$_3$, has a high acute toxicity. By contrast arsenobetaine (CH$_3$)$_3$As$^+$CH$_2$COO$^-$, an organoarsenic derivative often found in fish and seafood, is virtually non-toxic. The arsenic is masked by four stable carbon bonds and is not easily metabolised. A threshold limit for total arsenic cannot be justified because it does not reflect the risk associated with the concentration of arsenic in food. It might be suggested that a threshold for total arsenic in food should be based on inorganic arsenic as a precautionary measure. This is unrealistic because fish and other seafood would then be phased out if the guideline value of 1 mg arsenic/kg is exceeded – even though these foods are perfectly safe to eat. The choice of a threshold value for arsenic in food therefore depends upon accurately identifying the speciation of any arsenic present.

Analysis of arsenic species in food

Validated analytical procedures have not been established to identify and quantify all the arsenic species in food. The reason for this is that no Reference Materials with certified levels of the relevant arsenic species are available. Also, we still lack information on the identification and quantification of arsenic species in the biota. This is due to inadequate identification AND quantification methods, which do not respect the instability of different arsenic species during sample preparation and separation [1].

Analytical techniques. In assessing the problems and limitations of the established methods for arsenic speciation analysis, we have developed state-of-the-art analytical procedures for the identification of arsenic species in food. Traditionally arsenic species have been identified solely by retention time comparisons with standards – using ion exchange HPLC procedures coupled to arsenic-selective detection techniques such as atomic fluorescence spectroscopy (AFS), atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) spectrometry. Recently inductively coupled plasma mass spectrometry (ICP-MS) has become popular because it has the necessary sensitivity and selectivity and, most importantly, chromatographic techniques can be coupled on-line to an ICP-MS.

Inductively coupled plasma mass spectrometry. In the harsh ionisation conditions of the plasma, molecules disintegrate rapidly and readily form single charged element ions, which are separated by their mass over charge ratio and then detected. Arsenic is mono-isotopic at m/z 75 and does not suffer from isobaric interferences from isotopes of other elements. However, a molecular cluster such as ^{40}Ar^{35}Cl$^+$can interfere, and its formation has to be monitored by other mass/charge channels e.g. m/z 77 (^{40}Ar^{37}Cl$^+$). The signal intensity of an element is mostly independent of the molecular species prior to ionisation. This enables quantification to proceed without the need to use identical standard species – due to the fact the ICP-MS has an element-specific response rather than a molecular-specific one. This feature is very useful, especially for the quantification of arsenic compounds from biological samples, which often contain unknown or unstable arsenic species.

ICP-MS is also a very sensitive technique, which often achieves detection limits of a few nano- or picograms per sample volume or mass. Despite its low detection limits, the use of ICP-MS as detector for arsenic speciation has some drawbacks. Among these is a complete loss of molecular information – which means that species have to be identified by retention time and comparison with a known standard when coupled to HPLC. This presents a problem when biological samples are analysed, since known and well-characterised arsenic species are rarely available. However, by coupling the chromatographic method (e.g. HPLC) to a molecular mass spectrometric technique such as electrospray mass spectrometry (ES-MS), molecular information is conserved.

Electrospray mass spectrometry (ES-MS). In contrast to ICP-MS, ES-MS reveals the molecular mass of the protonated molecule (in positive mode), and depending on the instrument used, it can give information about molecule fragments formed in the high vacuum of the instrument. ES-MS has often been described as a soft ionisation method. For small molecules, one proton is transferred onto the neutral sample molecule producing a single charged cation. For larger molecules, multiple protons add on producing multiple charged cations. These are separated by their mass to charge ratio (m/z) from other molecules. However, extracts of biological samples contain a mixture of a large number of organic compounds resulting in multiple peaks with similar m/z ratios as the arsenic species.

Combined MS techniques. If we combine these two mass spectrometric techniques and couple HPLC-ICP-MS with ES-MS, we are able to identify and quantify arsenic species among the various organic compounds in biological extracts. ICP-MS identifies the eluting arsenic-containing species and their molecular fragments, which have been generated by ES-MS. As an example of this approach, **Figure 1** shows the first identification of an organothioarsenic species in urine.

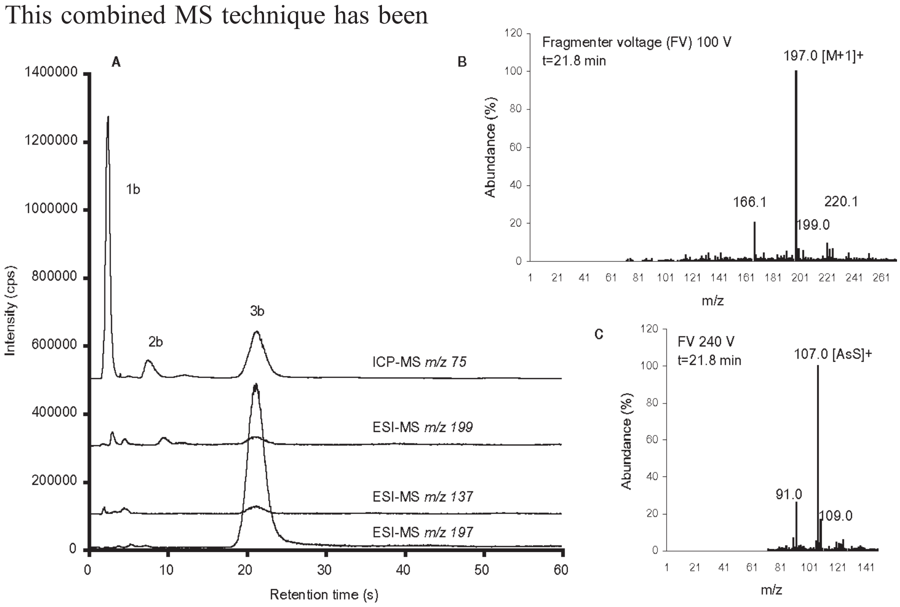

Figure 1: *Separation of newly identified arsenic species (3b, dimethylarsenothioyl acetic acid) in urine by using strong anion exchange chromatography (PRP X-100 Hamilton) coupled to ICP-MS for arsenic selective detection (m/z 75) and parallel to ESI-MS for the protonated molecular mass (m/z 197, 199) and major fragments (m/z 137) B: gentle ionisation at 100 V C: molecular fragments of m/z 107,109 (As=S) and m/z 91 (As=O) at 240 V fragmentor voltage (H. R. Hansen et al. Angew. Chem. Int. Ed., **43**, 337-340 (2004)).*

This combined MS technique has been examined in several projects where the transformation of arsenic species takes place in the environment. Two of these projects are described in more detail in the remainder of this article: (a) the biotransformation of arsenosugars by sheep and (b) the uptake, transformation and translocation of arsenic in plants.

Biotransformation of arsenosugars by sheep

Arsenic in seaweed. Seaweed can contain up to 200 times the guideline limits for arsenic in foodstuff, e.g. *Laminaria digitata*, commonly called kelp, contains around 70 mg arsenic/kg dry mass. However, the main arsenic species are neither the toxic inorganic arsenic species nor the non-toxic arsenobetaine; the arsenic is bound mainly to ribose derivatives as arsenosugars.

Although arsenic is known to accumulate in seaweed naturally, these macroalgae are still widely used as fertilisers by organic and traditional farmers, and as ingredients in traditional cuisine around the world. Many Asian dishes, for example sushi, contain significant amounts of seaweed. Closer to home, national dishes such as Welsh laverbread and Irish dulse both consist mainly of red seaweed species, which contain more than 10 mg/kg arsenic in the form of arsenosugars.

More than fifteen naturally-occurring arsenosugar derivatives have been identified, mainly from marine sources. The acute and chronic toxicities of these arsenosugars are poorly understood and their metabolism also needs to be elucidated.

Arsenic metabolism in seaweed-eating sheep. In order to study the metabolism of arsenosugars, we have identified arsenic-containing metabolites in the urine of the famous seaweed-eating sheep from North Ronaldsay in Orkney. These sheep belong to a rare breed of primitive sheep and are kept on the beach, a tradition which goes back centuries. The sheep have adapted to a diet of nearly 100% kelp [2]. The sheep eat more than 1.4 kg seaweed daily and consume nearly 35 g of arsenic per year – almost a world record for any terrestrial mammal.

Arsenosugars in kelp [3] are absorbed by the Orkney sheep and undergo metabolism in the liver to a number of products shown in **Figure 2**. This study identified many of these arsenic metabolites for the first time [4]. Most of the metabolites are water-soluble and excreted in the urine. A half-life of about 17 h indicates that the transformation of arsenosugars into the water-soluble arsenic metabolites is a time consuming process.

Although the arsenic is bioavailable, and dimethylarsinic acid [$(CH_3)_2AsO(OH)$; DMA(V)], the main breakdown product, is known to be a co-carcinogen, the toxicities of the other metabolites (and

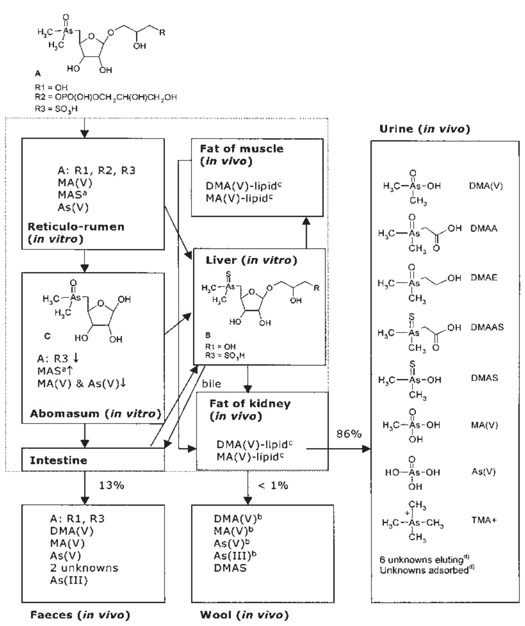

Figure 2: Metabolic pathway of arsenosugars, the principle arsenic compounds in seaweed, and their metabolites in North Ronaldsay sheep (H. R. Hansen, PhD thesis, University of Aberdeen, 2004).

Figure 2: *Metabolic pathway of arsenosugars, the principle arsenic compounds in seaweed, and their metabolites in North Ronaldsay sheep (H. R. Hansen, PhD thesis, University of Aberdeen, 2004).*

in particular the organothioarsenicals) have not been established [5,6].

This study in sheep has proved to be relevant to the human consumption of seaweed. Most human urinary arsenic metabolites identified after consumption of a seaweed-based meal are identical to those found in the Orkney sheep – indicating the relatively insignificant influence of rumen bacteria of the ruminants in arsenic metabolism. The contrast between the complexity of arsenosugar metabolism and the metabolism of inorganic arsenic makes it difficult at present to establish arsenic species-specific threshold levels for food.

Uptake, transformation and translocation of arsenic in plants

Plant metabolism. The second example concerns the biotransformation of arsenic in the soil/plant environment. When seaweed is used as fertilizer, arsenosugars leach into pore water and are transformed within a few weeks into toxic inorganic species – arsenite and arsenate. Inorganic arsenic can accumulate in soil and be absorbed by crops.

How plants absorb and accumulate arsenic, and transform and translocate the metalloid within the plant present mechanistic challenges [7]. Once these processes are fully understood, preventative measures can be taken to perhaps allow arsenic-containing water for irrigating plants – without increasing the risk associated with higher level of arsenic in crops.

What arsenic species are formed in the plant after arsenic uptake? And how might these species influence the amount of arsenic transported from the roots to the leaf or grain?

Phytochelatins. Larger labile complexes of arsenic with polypeptides may be formed in the plants. In particular, cysteine-rich phytochelatins (PCs) are thought to influence the tolerance of the plants towards metals and their ability to accumulate and translocate arsenic from the roots into leaves and grains. Plants increase their production of PCs when they are exposed to high levels of potentially toxic elements (PTEs) such as copper, zinc and arsenic. Whether arsenic complexes are actually formed and if these then prevent the translocation of arsenic is not completely clear at present.

Analysis of arsenic PC-complexes. Arsenic PC-complexes are unstable under the influence of oxygen and disintegrate into the peptide and arsenite, which is then partially oxidised to arsenate. We have developed sample preparation and chromatographic techniques, which conserve the integrity of the complex. Reverse-phase chromatography at low temperature (+6 ˚C) using methanol and/or acetonitrile in formic acid followed by the combined MS techniques described previously allow the identification and quantification of arsenic PC-complexes [8].

Studies on **tolerant arsenic plants and arsenic hyperaccumulators** such as ferns (*Pteris* spp.) have revealed that most arsenic in the roots are actually bound as arsenite and arsenate, while **arsenic in non-tolerant plants** such as *Holcus lanatus* or *Helianthus annuus* show higher amounts of arsenic bound to PCs (**Figure 3**) [9]. The analysis of xylem sap showed that arsenic was transported in its free inorganic form or as a labile complex rather than as As-PCs, while the leaves contain As-PCs in significant amounts. This work has uncovered the diversity of As-PCs complexes found in the plant kingdom. But further investigations are needed before extrapolating these findings to crops grown in Bangladesh and Vietnam, which are irrigated with arsenic-containing water.

Summary

Arsenic is thiophilic and forms relatively strong As-C bonds, which explains the diversity of arsenic speciation in nature. Biotransformation of arsenic species can occur on different levels and determines the behaviour of the element in the environment. Only when reliable analytical data are available, and toxicological assessments have been made of the diverse arsenic species, can food safety regulators advise more precisely on the maximum allowable arsenic levels in food.

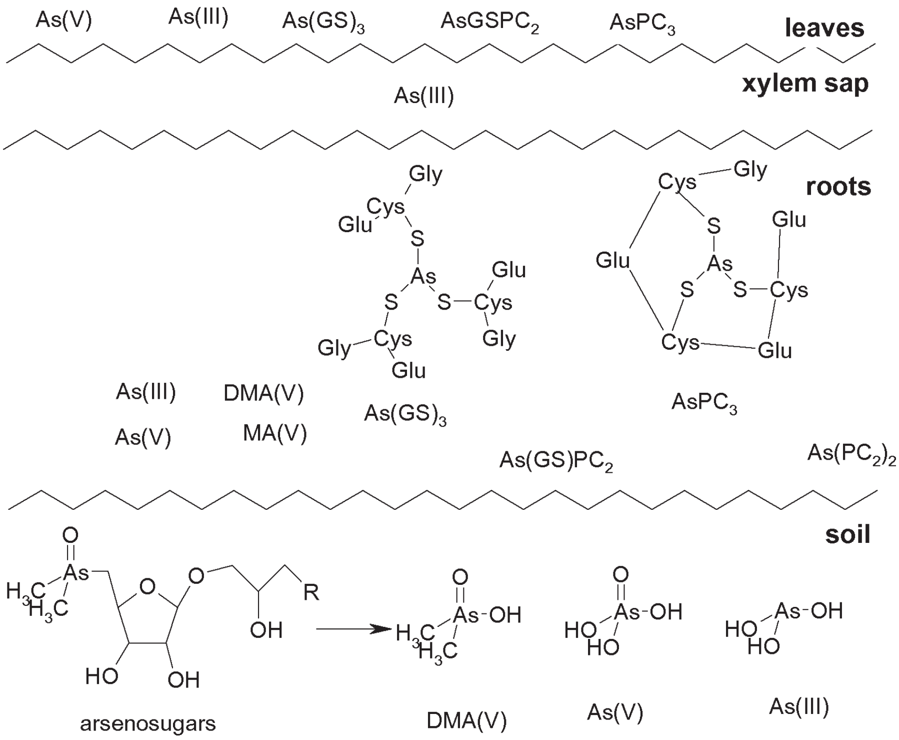

Figure 3: Transformation of arsenosugars from seaweed fertilizer in soil and the uptake, transformation and translocation of arsenic in plants from the roots to the leaves, e.g. sunflowers.

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Some other recently published papers from Prof. Feldmann's research group on arsenic speciation:

A. Raab, H. Schat, A. A. Meharg, J. Feldmann. Uptake, translocation and transformation of arsenate and arsenite in sunflower (*Helianthus annuus*): formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations. *New Phytologist*, **168**, 551-558 (2005).

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This article is an edited version of Professor Feldmann's talk at the ECG 2005 Distinguished Guest Lecture and Symposium.

A wild North Ronaldsay sheep standing in its staple food of seaweed (L. digitata)


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The use of dried hyacinth roots to remove arsenic from surface water

Introduction

High doses of arsenic (As) are known to be toxic to humans, but chronic, long term exposure to inorganic arsenic can also be detrimental to health. Exposure to low concentrations of As can affect the gastrointestinal tract, respiratory tract, skin, liver, cardiovascular, haematopoietic and nervous systems. Some of these human health effects are currently being observed in populations in Argentina, Bangladesh [1], China, India, Mexico and Taiwan [2] where the drinking water is contaminated by arsenic. The WHO guideline value for arsenic in drinking water is 10 mg l^{-1} [3]. The US EPA recently approved new guidelines, which will phase in a maximum contaminant level of 10 mg l^{-1} [4]. In Bangladesh alone, more than 60% of the ground water contains arsenic concentrations greater than the WHO recommended value [5] and this is estimated to affect the health of millions of people.

A range of different methods can be used for the removal of arsenic from drinking water and patents protect a number of these technologies. A selection of different approaches to this problem includes the use of: natural zeolites [6]; ion exchange resins [7]; natural products, such as chitosan and chitin [8]; fly-ash [9]; and activated alumina and other oxides [10, 11]. However, cost effective, straightforward methods are necessary for the people in developing countries, particularly technologies utilising materials that are widely available. Nikolaidis *et al*. [12] suggested a simple filter using sand and iron fillings, which was based on the precipitation of arsenic with iron. Other potential approaches would include the use of phyto-remediation, whereby green plants are used to remove pollutants from the environment and render them non-available [13] or rhizofiltration, defined as the use of plant roots to absorb, concentrate and precipitate metals from solution [14]. Several plant species are known to accumulate metals from the environment [15, 16, 17, 18], including water hyacinth (*Eichhornia crassipes*), which grows in waterways in many parts of the world and has been used as a model system for studying the uptake of metal ions by aquatic plants [19, 20, 21, 22, 23]. These studies employed living plants, which were not shown to be highly effective in removing arsenic [24]. In contrast, there are two studies, which report that living plants can be effective in removing arsenic from water [25, 26]. The use of biomaterial derived from non-living dried water hyacinth roots may be a more convenient and effective method for the removal of toxic metal(loid)s. Although some studies have been reported on the use of dried plant material as a potential industrial tool for metal removal [27, 28], these studies have not focused on the removal of arsenic from aqueous solutions.

An appropriate technology for arsenic removal, particularly in the context of less developed countries, should address the following criteria: (1) the technology must be of simple design and easily produced; (2) it must be low cost; (3) it must use local, easily accessible materials; (4) it must have a rural focus [16]. This study presents data on the potential of using a biomaterial derived from dried water hyacinth roots as a way to remove arsenite and arsenate from aqueous solution. This could be a simple yet effective means to reduce the As content of surface water in many developing countries, like Bangladesh and India, where this plant is available in abundant supply.

Materials and methods

Sample preparation. Water hyacinth (*Eichhoria crassipes*) plants were collected from a pond in Dhaka, Bangladesh. The plants were thoroughly washed with deionised water before being left to air dry before being returned to the laboratory. The roots were subsequently pulverized in a laboratory blender mixer to obtain a fine powder.

Instrumentation. Graphite–furnace atomic absorption spectroscopy was used in conjunction with Zeeman background correction to determine the uptake of arsenic. The detection limit (*DL=3 x SD*) for arsenic was 0.25 mg l^{-1}.

Experimental procedure. A specific weight (750 mg) of water hyacinth root powder was suspended in 25 ml of a 200 mg l^{-1} solution of arsenite [As(III)] or arsenate [As(V)] at pH 6. The mixture was shaken for 120 minutes in a horizontal shaker at room temperature. At different time intervals, the roots were removed by filtration to obtain the supernatant solution, which was analysed by GF-AAS.

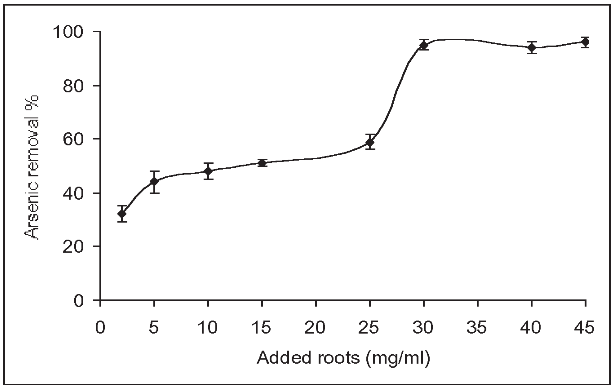

***Figure 1:** The effect of varying the mass of water hyacinth roots on removal of arsenic from a 200 µg As l^{-1} solution at pH 6.0 after 1hr exposure.*

Results and discussion

The dried water hyacinth roots were tested using a static batch system rather than using columns packed with the material, because this eliminated a number of problems related to column blockage, non-equilibrium conditions and uncertainties associated with non-uniform flow in such a dynamic system. To determine the most appropriate mass-to-solution volume ratio to use in the experiments a range of different test solutions were prepared, containing a fixed volume of arsenate (200 mg l^{-1}), but with increasing mass (2 to 45 mg ml^{-1}) of root material. The results shown in Figure 1 indicate that quantitative removal of arsenate from solution at pH 6.0 was achieved in 60 minutes, using between 30 to 45 mg ml^{-1} of dried root material. A mass-to-volume ratio of 30 mg roots ml^{-1} solution was therefore adopted in the further batch experiments used to evaluate the material as a bioadsorbent.

The removal of arsenite and arsenate from aqueous solution using dried, non-living, water hyacinth root powder as a function of time is shown in Figure 2. Over 80% of the arsenic was taken up within 30 minutes exposure and 96% of both chemical species of arsenic were removed within two hours, leaving a solution containing less than 10 mg l^{-1},

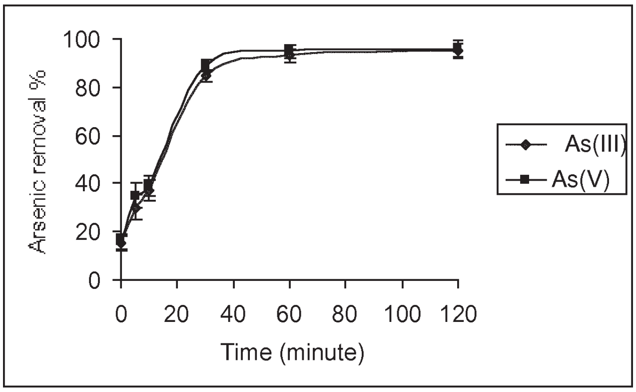

***Figure 2:** Arsenic(III) and arsenic(V) removal by dried water hyacinth roots as a function of time (30 mg roots ml^{-1} at pH=6.0 and 200 µg As l^{-1} as the initial metalloid concentration in solution.*

the WHO guideline value. The removal rate was rapid within the first 20 minutes, slowing down between 20-40 minutes and then gradually approaching equilibrium after 40 minutes. This could be due to two different sorption processes, a fast ion exchange process followed by chemisorption, similar to that which has been previously suggested for sorption of lead and cadmium by non-living water hyacinth roots [28].

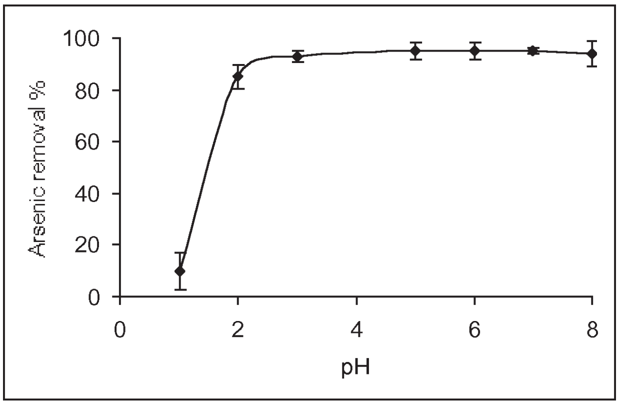

***Figure 3:** The effect of pH on arsenic removal by dried water hyacinth roots, 30 mg roots ml^{-1}, using a constant concentration of 200 µg As l^{-1}, for a total contact time of 4 h.*

Arsenic removal varied with the pH of the aqueous solution (Figure 3) and was optimal between pH 2.5 and 8.0, which covers the normal pH range for water. The low percentage removal at pH 1.0 cannot be readily explained because of the limited characterization of the material that was undertaken during this initial study. However, it has been reported [28] that water hyacinth roots are negatively charged due to the presence of carboxylate, sulphate, amino and other groups on the root surface. At low pH neutralisation of the negative groups on the root surface, as a result of interaction with H$^+$ ions, will reduce the number of negatively charged groups available for interaction with positively charged metal ions. This could result in desorption of the cations present on the surface which will then be available to complex with the oxyanionic arsenic species present in solution. The exact chemical speciation of the soluble inorganic arsenic will also be dependent on the prevailing pH (and pε) conditions. Under the redox conditions present in this experiment both arsenic oxidation states will be present as the corresponding oxyanion species and these will vary in protonation with pH. At lower pH values both species will be fully protonated and exist as the non-ionised acid.

The need for materials to remove arsenic from waters used for drinking and irrigation of crops has been recognized for a number of years and many different materials have been developed for this purpose. Some natural zeolites from Mexico and Hungary were investigated for removing arsenate (As(V)) from aqueous solution [6]. After 5 days contact time with different spiked water samples both zeolites removed 75% of the 200 mg l^{-1} added arsenate. A chitosan and chitin mixture was shown to remove As(V) from groundwater [8] and the capacity of the mixture at pH 7 was recorded to be 10 µg of arsenic per gram of mixture. Precipitation with iron oxides and hydroxides is another processes commonly used for treating water in some parts of the world affected by As. Recently, Katsoyiannis *et al.* (2004) [29] have reported the use of a combination of iron and oxidizing bacteria to remove 65% of As(III) from solutions containing initial arsenic concentration over 150 mg l^{-1}. In comparison to these approaches the biomaterial reported herein achieved better results than the zeolites in a shorter time period, had a 5-fold better removal efficiency than the chitosan/chitin mixture and a higher efficiency compared to the iron precipitation method.

Water hyacinth is considered to be an environmental "plague" throughout many tropical and subtropical parts of the world and in Bangladesh, and India, the plant grows abundantly in ponds, lakes and rivers. It has been reported [28] that water hyacinth biomass can be produced at a rate of 160 to 1000 Kg hectare^{-1} day^{-1} depending on the nutrient and temperature conditions. In this study, the water hyacinth roots exposed to 1500 µg As l^{-1} (Figure 4) removed up to 50 µg As g^{-1}of roots. Assuming an arsenic solution concentration of 1500 mg l^{-1}, approximately 30 grams of dried roots would be required to remove 1500 µg of arsenic from 1 litre of water over a 24 hour time period. Therefore, to treat 1000 litre of water 30 Kg of roots would be required. This would be sufficient to provide the drinking water needs of a village consisting of hundreds of people. Production of this biomaterial is inexpensive and the raw material is widely available. The dried powder could be used to produce cheap filters to be used by people that do not have access to more expensive alternatives. Bearing in mind the poor infrastructure of most developing countries, it is essential to find low-cost techniques suitable for the removal of toxic elements from drinking and irrigation waters in rural areas. The use of dried water hyacinth roots may be

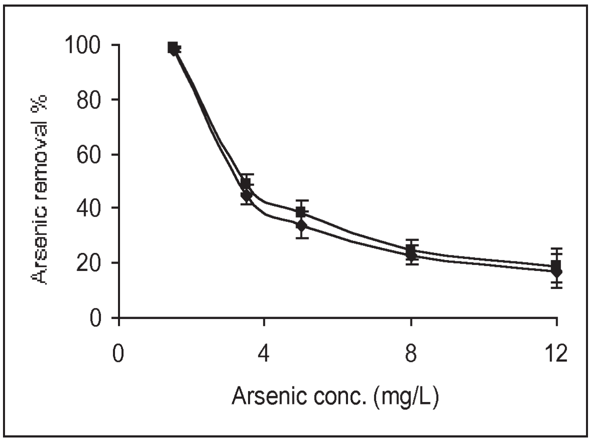

***Figure 4:** Arsenic removal by dried water hyacinth roots as a function of arsenic concentration at a constant mass of water hyacinth roots (30 mg roots ml^{-1}, at pH 6.0 and after 24 h of exposure).*

one way to achieve this goal.

Conclusions

This initial work has highlighted the potential for using dried plant materials to remove arsenic from surface waters. The hyacinth plant used is widely available in many of the areas affected by high levels of arsenic in the drinking water and has often been referred to as a "plague", because of its growth rate and persistent nature. The envisaged filter technology would fit all of the criteria detailed in the introduction for the removal of As in the context of a developing country. In further work we hope to investigate the mechanisms of absorption, the quality and safety of the remediated water, possible disposal mechanisms for the contaminated waste and ultimately the development of a suitable filter. We are currently endeavouring to find funding for these investigations.

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This article is based on a paper in *Journal of Environmental Monitoring*, 2005, **7**, 279-282, and is published by kind permission of the Royal Society of Chemistry. Chris Harrington is a committee member of the Environmental Chemistry Group.

Monitoring of ambient air particulate arsenic concentrations at nine sites in Cornwall

Introduction

Cornwall's history of mining and smelting has left a legacy of contamination and pollution. Between 1860 and 1900 Cornwall was the world's major producer of arsenic and at the height of the industry also imported arsenical ores for smelting. As a result of this activity soil in some parts of Cornwall has the world's highest concentration of arsenic (up to 2500 ppm(m)). Elsewhere in the UK and the rest of the world (but with notable exceptions) soil arsenic concentrations are usually below 40 ppm(m) (WHO 2000). Because of perceptions in Cornwall about the hazard posed by developments that may resuspend arsenic contaminated soil, interest has been focused on airborne PM_{10} arsenic concentrations.

For 'normal' UK environments (in 2000) The Department for the Environment, Food and Rural Affairs (DEFRA) gives annual mean airborne concentrations of arsenic in as being typically in the range of 1-4 ng m^{-3} whilst annual mean urban concentrations were higher, in the range of 5-7 ng m^{-3} (Maggs 2000) – these latter data relating to traditional metal smelting industries e.g. Walsall, West Midlands.

Other data relating to arsenic in ambient airborne particulate matter in the UK are available on the National Environment Technology Centre (NETCEN) website. However, there are no monitored sites in Cornwall. Unlike other regions in the UK for which historical data allows trends to be identified, there is no way of assessing whether trends in Cornwall show an increase or decrease in airborne particulate arsenic concentrations. A decrease is observed elsewhere in the UK (Maggs 2000) but as indicated above, the situation in Cornwall is unique.

This project is focused on concerns about human exposure through inhalation of arsenic-containing airborne dust and soil particulates. It has particular relevance for situations where movement of soil or the proximity of exposed contaminated soil may cause problems of airborne particulate pollution which, because they are only indirectly related to initial assessments of risk, may well be overlooked.

This study presents a first attempt to do a localised study of PM_{10} associated with arsenic contaminated land. There were two specific tasks. First, to establish a background level of PM_{10}-arsenic in Cornwall against which fugitive dust-releasing activities around new developments can be assessed and second, to do a preliminary assessment of spatial variations in PM_{10}-arsenic across Cornwall so that if high exposure of residents to wind blown resuspended arsenic from historically contaminated land occurs then interventions can be made.

Methodology

Monitoring took place at nine sites in west Cornwall (Figures 1 and 2). The areas were classified as being with or without an extensive mining history on the basis of information from historical mine site maps (CCC 2005) – this was to reveal any differences between the two site classes in relation to resident exposure (Table 1).

Airborne arsenic was sampled using a gravimetric Partisol model 2000 Air Sampler fitted with a SA246b PM_{10} inlet head (serviced by Air Monitors™). The Partisol collected respirable particulate matter less than 10 μm (PM_{10}) on to 0.8 μm 47 mm cellulose nitrate filters. These filters were analysed using ICP-MS at Royal Holloway, University of London and by QEMSCAN™ by Camborne School of Mines (CSM) Tremough campus. An Osiris particulate monitor (Turnkey Instruments) was also used together with a DustScan particulate collection device. The Osiris monitored continuous Total Suspended Particles, PM_{10}, $PM_{2.5}$, and $PM_{1.0}$ mass fractions but did not retain samples for further analysis. Continuous data obtained by the Osiris was compared to wind data to allow directional correlation of particulate concentrations throughout the monitoring programme. The Dust Scan consists of an adhesive dust collection sheet mounted on a cylinder on a 2 m high stand. The monitoring head collects fugitive dust from 360° on a sheet which can then be analysed to identify the direction from which deposition occurred to determine the nature of the deposits. DustScan samples can be further examined by Scanning Electron Microscopy (SEM).

For the full programme monitoring nine sampling sites were chosen within an area of west Cornwall. The sites were chosen with specific reference to several criteria, namely:

- Relevance to residential areas
- The proximity to historic mining or mining-related waste sites
- Exposures to all wind directions (open aspect)
- The provision of a power supply and security.

Location	***Site No.***	***Proximity to mining site***	***Type***
Tuckingmill (Camborne)	1	200 m	Town centre
Porthtowan	2	300 m	Edge of village
Stithians	3	2500 m	Rural
Bissoe	4	400 m	Rural
Trelissick	5	3500 m	Rural
Carharrack	6	500 m	Edge of village
Falmouth	7	1500 m	Town centre
Constantine	8	2000 m	Rural
Crowan	9	700 m	Village centre

Table 1: *Location of the 9 sites in west Cornwall chosen to monitor arsenic in air*

Figure 1

Monitoring took place between June and August 2005. The dry summer months were monitored as this period (because of high pressure events) is known from previous monitoring in Cornwall to be most likely to yield localised re-suspended dust. Each site was monitored for a 2 week period which collected 4 filters, each exposed for 72 hours sequentially.

Results

Filter analysis

ICP-MS filter analysis performed by Royal Holloway, University of London, showed arsenic concentrations to be values in the range 0.08 – 2.78 ng m^{-3}. The lowest values from the analyses are at the limits of detection and the highest values agree with annual mean concentrations of arsenic in the UK rural environment (1 – 4 ng m^{-3}) (Maggs 2000). Most concentrations are below this range and all are well below the EU Air Quality guidelines of 6 ng m^{-3} (EC 2001); European Commission 2001. Figure 3 shows the site average concentrations of airborne arsenic over the whole monitoring period.

In spite of the visual suggestions of a spatial trend in relation to 'mine' and 'non-mine' sites, the filter analysis results showed no significant statistical differences between any of the monitoring sites. Although this may be linked due to the low number of samples and the high degree of variation between samples at the same sites, it does reflect the current state of knowledge as regards ambient PM_{10}-arsenic in Cornwall.

Figure 2

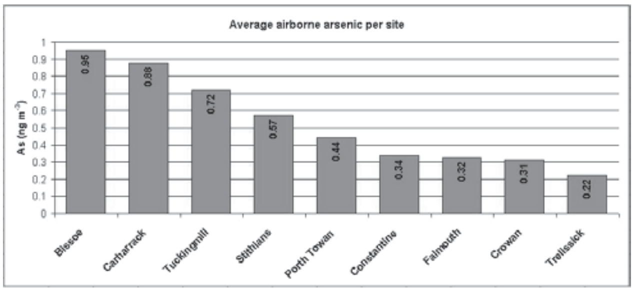

Figure 3

Rapid quantitative mineral and phase analysis using automated scanning electron microscopy (QEMSCAN™)

One filter from each site was chosen for further analysis to determine whether the arsenic concentrations identified by ICP-MS analysis were made up of several small particles or fewer larger ones. QEMSCAN™ analysis performed by CSM identified a total of three arsenic particles from a total of >91,000 particles. All three particles were identified on the filter from the Carharrack sample site (second highest concentration of arsenic identified by ICP-MS analysis). Two of these As-bearing particles were arsenopyrite whilst the third was a mixture of arsenopyrite and Fe-oxides. The most likely source of this type of arsenic is anthropogenic e.g. modern mine tailings. The lack of arsenic particles identified by QEMSCAN™ analysis maybe due to the particles being smaller than the resolution/pixel spacing (0.5 μm) set on the machine. This puts the other arsenic containing particles into the ultrafine category. This ultrafine category is the most inhalable and therefore potentially the most dangerous.

Future study

This investigation has highlighted the potential for further studies examining the effects both of particulate resuspension associated with specific development activities. Next year's monitoring will build on these preliminary findings.

Acknowledgements

The Air Quality Unit at Cornwall College would like to acknowledge the Environment Agency and the European Social Fund for their funding contributions to this investigation. We would also like to thank the site hosts who housed the monitoring equipment and the Universities of Exeter (Cornwall School of Mines), Plymouth (Electron Microscopy Centre) and London (Royal Holloway) for filter analysis.

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This programme is part funded by the European Union through the European Social Fund – helping to develop employment by promoting employability, business spirit and equal opportunities and investing in human resources.

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Forthcoming symposium

Impact of climate change on air quality

Royal Society of Chemistry Environmental Chemistry Group

2006 Distinguished Guest Lecture & Symposium

To be held in the **Council Room** of the **Royal Society of Chemistry** on Wednesday 1st March 2006

The 2006 Distinguished Guest Lecturer will be **Professor Mike Pilling**, University of Leeds

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

The nearest Tube stations are Green Park and Piccadilly Circus

Symposium & Distinguished Guest Lecture

Impact of climate change on air quality

PROGRAMME

13.30 Chairman's Introduction: Dr Brendan Keely (Chairman, RSC Environmental Chemistry Group)

13.35 Dr Hugh Coe, University of Manchester
Aerosols, air quality and climate

14.20 Dr Guang Zeng, University of Cambridge
Impacts of climate change on tropospheric composition

15.05 Tea and **RSC Environmental Chemistry Group Annual General Meeting**

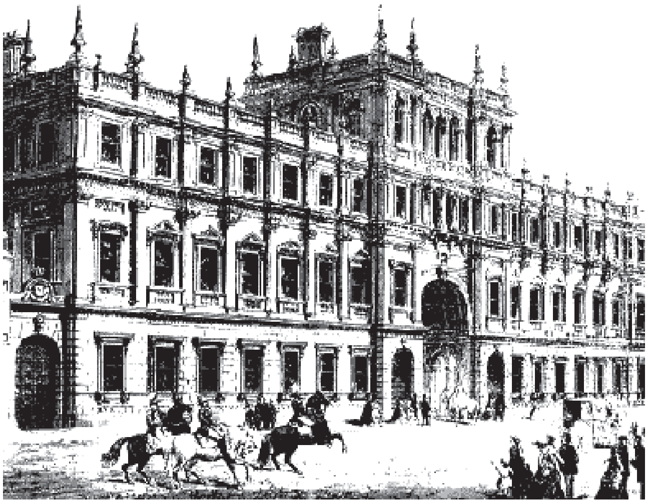
15.30 Introduction to the 2006 Lecture and presentation of the DGL Medal

15.35 **2006 RSC Environmental Chemistry Group Distinguished Guest Lecture:** Professor Mike Pilling, University of Leeds
Climate change and air quality – A chemist's perspective

16.35 Open Forum

17.00 Close

Admission is by ticket only. In order to register for this meeting, complete the slip below and return the completed reply slip to Dr Michael Leggett by post. Members of the ECG may also register by email. Guests are welcome and there is a charge of **£25** for non-members of the Environmental Chemistry Group, which should be returned with the slip (cheques made payable to *RSC Environmental Chemistry Group*). **Early application is encouraged as places are limited and will be allocated on a first come first served basis.**



*The entrance to **Burlington House** from Piccadilly, from a drawing dated 1871. Venue for the ECG 2006 Symposium & Distinguished Guest Lecture.*

ROYAL SOCIETY OF CHEMISTRY, ENVIRONMENTAL CHEMISTRY GROUP

Thirty-third Annual General Meeting, 1st March 2006 and Distinguished Guest Lecture & Symposium on *Impact of climate change on air quality*

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British Standards Institution, 389 Chiswick High Road, London W4 4AL

Royal Society of Chemistry Environmental Chemistry Group Distinguished Guest Lecturer Medal

From its early days, the Environmental Chemistry Group has made a special feature of the Annual General Meeting, by inviting a person well known in the environmental arena to present a **Distinguished Guest Lecture** (DGL). In 1990, the AGM was further enhanced by adding a supporting half-day programme to the Distinguished Guest Lecture. In the 1980s, two notable lectures were given by Sir Derek Ezra and by Sir Walter Marshall on the environmental problems relating to the coal and gas industries respectively. Other speakers in that decade included Sir Richard Doll (1986), Sir Jack Lewis, then Chairman of the Royal Commission on Environmental Pollution (1987), and Sir John Mason, Director of the Meteorological Office, (1988).

The wide-ranging environmental topics discussed at the DGL continued in the 1990s with presentations from Professor Roger Perry, Imperial College, (1990) on toxic waste management, Professor Paul Crutzen (1991) on global atmospheric chemistry, and the meteorologist Sir John Houghton, who was invited to give the DGL in 1993 and in 2000. Over the last decade, Distinguished Guest Lecturers have included Professor Roy Harrison (1996), Professor Mario Molina (1999), Professor Peter Liss (2002), and Professor Jane Plant (2005).

RSC ECG DGL Medal

In 2006 the Distinguished Guest Lecturer will be Professor Mike Pilling from the University of Leeds. At the 2006 DGL, the inaugural award of the ECG's **Distinguished Guest Lecturer Medal** will take place. This medal will be presented from 2006 onwards to the ECG Distinguished Guest Lecturer.

The Distinguished Guest Lecturer Medal was cast from Cornish tin and smelted and refined using traditional methods to around 99.6% purity. The tin was won before the closure in 1998 of South Crofty Mine, West Cornwall (the last working tin mine in the UK), and produced by the South Crofty Collection. The medal was designed by Patrick Lowry MA who lectures in the Cornwall College Fine Art Department. He chose the water molecule as a motif because of the ubiquity and uniqueness of water and its intimate relationship with environmental issues. A superimposed tetrahedron symbolises the carbon cycles through which life on earth flourishes and declines.

The medal is decorated with a gold and black ribbon (the Cornish colours) and will be presented in a mahogany box, designed by Phillip Whitfield MA and made by students from the Cornwall College's Furniture Design Foundation Degree.

Patrick Lowry, Cornwall College

Jo BARNES and **Leo SALTER**
Cornwall College

News of the ESEF

The Environment, Sustainability and Energy Forum (ESEF) was set up in 2003 with a remit to set, drive and deliver the strategy for environmental, sustainability and energy issues within the RSC. ESEF currently is running initiatives in four key priority areas, Sustainable Energy, Sustainable Water, Chemistry of the Natural Environment and Green Chemical Technology.

Notable achievements in 2005 include:

- **Parliamentary Links Day** was this year themed around 'The Science behind the G8 Summit' concentrating on the Government's twin priorities of Climate Change and Africa and was attended by the Rt Hon Tony Blair MP. Dr Andrea Jackson (ESEF vice-chair and ECG committee member) gave a key presentation at the event (please see www.rsc.org/ScienceAndTechnology/Parliament/);
- The launch of "**Chemical Science Priorities for Sustainable Energy Solutions**" report (please see www.rsc.org/Membership/Networking/InterestGroups/ESEF);
- The launch of "**How to Plug the Energy Gap**" report following the **Challenges and Solutions – UK Energy to 2050** that ESEF co-sponsored (see above link);
- **Future Nuclear Power** and **Climate Change** were both topics for successful and well attended Science and Technology policy seminars adding to the reputation of the RSC as an honest broker in scientific debate.

ESEF has also been involved in the organisation of and/or sponsored a number of other conferences, meetings, workshops and events throughout 2005.

Looking towards 2006, ESEF has a busy programme of initiatives planned including events focussing on atmospheric chemistry; a carbon capture and storage workshop; a report on sustainable water and international conferences on sustainable energy (2007) and biorefineries (2006). Your suggestions for future ESEF activities would be greatly appreciated.

For more information about ESEF please contact Dr Jeff Hardy (email: hardyj@rsc.org; tel: +44 (0) 20 7440 3395).

New book

Nitrate, Agriculture and the Environment

20% discount for ECG Members

Editor: T. Addiscott, Rothamsted Research, Harpenden, UK

This book addresses the widespread public concern about the effects of nitrate derived from farming, on water quality and public health. It begins by examining the reasons for nitrogen fertilizer use and how nitrate escapes from arable and grassland systems. The book then moves on to discuss ecological changes in coastal and estuarine water caused by nitrate, and the threat to the ozone layer caused by nitrous oxide. It also reviews the existing research on the effects of nitrate on health. The book builds on *Farming, Fertilizers and the Nitrate Problem* (CABI, 1991) by Addiscott, Whitmore and Powlson, and has been revised to take account of new developments and to bring out more clearly the role of politicians and economists in the 'nitrate problem'. It concludes that there are wide discrepancies between public perceptions and reality.

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Uranium in UK stream sediments, soils and stream waters

Background

The natural concentrations of uranium in stream sediments, soils and waters are controlled both by the occurrence of uranium in the underlying rocks (typically but not exclusively the sediment and soils parent material) and the subsequent mobility of uranium in the surrounding geochemical environment. These concentrations vary widely in a spatial context, depending on the source rock and its local weathering environment (e.g. soil redox potential (Eh), pH, [HCO_3^-]). For example, stream sediments associated with the uranium rich granites of Cumbria and Dumfries and Galloway have uranium concentrations in excess of 10 mg kg^{-1} (up to 800 mg kg^{-1}), whilst the regional median value is ~3 mg kg^{-1} (British Geological Survey, 1992; 1993).

Elevated concentrations of uranium in the environment are of concern due to the potential chemical and radiological risks to human and ecosystem health. And because uranium constitutes the primary source for the radioactive gas radon, which is considered to account for over 3,000 deaths per annum. Historically, concerns have been primarily associated with the activities of the civilian and military nuclear industries. However, more recently interest has focussed on the dissemination into the environment of depleted uranium (DU) due to its use in armour piercing weapons or high density ballast. This has also coincided with greater recognition of the importance of the chemical toxicity of uranium, as opposed to previously held perceptions of a purely radiological toxicity (Royal Society, 2001, 2002).

The principle diagnostic tool for evaluating the occurrence of nuclear fuel cycle uranium in natural environments is the measurement of the isotopic composition of the uranium. The isotopic composition of natural uranium in the Earth's surface environment is reasonably well constrained i.e. the $^{238/235}$U ratio being constant, with the single exception of the very ancient natural reactor at Oklo in Gabon; whilst the range of the $^{238/234}$U ratio is affected by leaching processes, preferentially removing ^{234}U from solid phases. The deliberate perturbation of the proportions of the respective isotopes is the basis for all nuclear fuel processing. When uranium is added to natural systems *via* the waste products of fuel cycle processes, it is most diagnostically reflected in variations to the $^{238/235}$U ratio, as this is virtually constant in nature. The incorporation of fuel cycle uranium wastes into the environment results in the superimposition of anthropogenic $^{238/234}$U on the natural $^{238/234}$U variation, making source apportionment more difficult than using $^{238/235}$U.

The British Geological Survey (BGS) has been contributing to the understanding of uranium sources, pathways and sinks for many years. This has involved all aspects from uranium exploration (from which the development of inductively coupled plasma–quadrupole mass spectrometry (ICP-QMS) technology was funded in the early 1980s), characterisation of candidate nuclear waste disposal sites in the 1990s for NIREX, to the detection and characterisation of depleted uranium projectiles.

This article summarises some of results from these studies that illustrate not only the ubiquitous nature of uranium in the UK environment but also the potential of modern instrumentation to unambiguously identify anthropogenic inputs.

Baseline (or ambient) concentrations of uranium

Mapping of the concentration of uranium, and a wide suite of other elements (at an average spatial resolution of around 1 sample per 2.5 km^2), has been undertaken at BGS for the last 30 years by the ongoing national survey "Geochemical Baseline Survey of the

Environment” (G-BASE) and its precursors. This survey of stream sediments began in the Orkneys and has systematically moved southwards to the present field study area of South East England. The addition of stream waters and soils to the sampling suite occurred more recently as the survey programme moved southwards, commencing in north-west England in 1989. However, importantly for this study, pH and dissolved uranium, fluoride and bicarbonate have been measured since the commencement of G-BASE sampling. This additional contextual data can be used to identify areas where greater dissolution and mobility of uranium form the solid phase may be expected. Summary results for quality assured data resident within the G-BASE database are shown in Table 1.

In addition to the regional survey data uranium has also been determined in urban soil samples (at a higher spatial resolution of 4 per 1 km^2). Urban environments surveyed to date include Swansea, Cardiff, Stoke on Trent, Hull, Sheffield, Nottingham, Derby, Leicester and Coventry. For a full description of sampled areas see http://www.bgs.ac.uk/gbase/home.html

	Soil	*Sediment*	*Water*
No. of Samples	38,537	100251	57912
Mean	2.4	4.0	0.001
Minimum	<0.5	<0.5	<0.0001
Maximum	76	3300	0.230
10th percentile	1.0	1.6	<0.0001
90th percentile	3.0	5.4	0.002

***Table 1:** Summary data for uranium concentrations determined in soil, stream sediment and stream water sampled from Scotland, Northern England and Wales (see Appendix 1) in units of mg kg^{-1} or mg l^{-1}*

Source identification and geo-forensics

Inspection of the G-BASE uranium concentration maps (Appendix 1) clearly allows the identification of regions containing naturally elevated concentrations of stream sediment, stream water and soil. Localised anomalously high levels of uranium can also be seen, which are not thought to be geological in origin. In the latter group, some appeared to be geographically associated with known uranium processing facilities at Drigg, Springfield and Capenhurst. While all of these sites have been licensed dischargers of uranium (e.g. MAFF, 1989; 1996; 1999), we found it particularly interesting that they could be so easily identified in these national scale studies.

To investigate these more localised observations, a pilot study was instigated with the primary aim of determining whether these anomalies were of natural or anthropogenic origin using uranium isotope ratio measurements. A limited suite of G-BASE stream sediment samples were selected, some that might contain uranium of anthropogenic origin due to their location and a control set of samples thought likely to contain only uranium of natural origin. These samples were subjected to a rapid acid leach to liberate potentially available uranium, but not uranium held strongly in detrital minerals such as zircon. With carefully attention to detail during the ICP-MS instrument optimisation, it proved possible to quantify an anthropogenic component of a few percent at background concentrations (~3 mg kg^{-1}) of uranium.

The resultant uranium isotope ratios were compared with values expected for natural, depleted and fuel cycle uranium and grouped accordingly (Appendix 2). As part of the regulatory process a government radiological monitoring program of environmental samples, collected from the vicinity of facilities handling nuclear materials, is conducted annually. The results of this survey are published in the Radioactivity in Food and the Environment (RIFE) reports. Data from this study have been compared to those published in 1989, 1996 and 1999 Similar patterns emerge but the superiority of the newer ICP-MS technology compared to the older radiometric measurements is clear.

This article was written by **Barry Smith** and **Simon Chenery** and summarises work previously published in BGS Technical Report IR/02/001 by Chenery, Ander, Breward and Smith (2002) and a number of regional geochemical atlases produced by the BGS G-BASE programme (see www.bgs.ac.uk). Appendices 1 and 2 are not reproduced in the printed version of this article, but may be seen in the Web version, which is available from the *ECG Bulletins* section of the RSC homepage: http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/bulletin.asp

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MAFF (1989; 1996; 1999) Radioactivity in Food and the Environment (RIFE) Reports

Web link: *British Geological Survey Mineral Profile: Uranium*, BGS, 2005 http://www.mineralsuk.com/britmin/uranium_nov05.pdf

Toxicogenomics and metal exposure

Toxicological responses

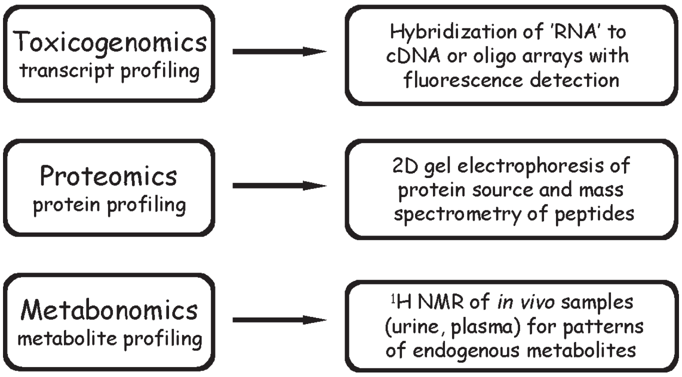
Traditionally, toxicology was concerned with observing the deleterious effects of drugs, pesticides and industrial chemicals, including heavy metals. With a greater understanding of molecular mechanisms and improvements in the sensitivity of analytical techniques, there has been a shift to elucidating mechanisms of, for example, carcinogenicity and genotoxicity. In recent years the possible adverse effects of low exposure to environmental agents, including organometallic compounds, has become important. In the future, concerns about low exposure effects of metals on neuronal development, including 'intelligence' and 'premature ageing' may become more prominent.

Any toxicological response is a complex interaction of timing, dose, species, sex and individual variation. Unfortunately prediction of responses in humans from those in experimental animals is fraught with difficulties. Even the influence of dose (exposure level) may not be straightforward. Biological response thresholds can be important factors – especially where receptors are involved. Individual variation in therapeutic responses to drugs is well established but toxic consequences may be more complex and very little is known about individual response to toxic metals. Recently, however, a gene for testicular susceptibility to cadmium has been found [Dalton *et al* (2005) *PNAS USA,* **102**, 3401]. Even for essential metals like selenium and iron, what constitutes a toxic level rather than a level for healthy life, is very complicated so that the degree and mechanisms of how other metals might interact with biological pathways are still relatively obscure. How to accommodate these complexities in assessing adverse human exposures to chemicals like metals is a challenging problem of epidemiology and technology.

Omics

Over recent years the complexity of experimental response to drugs and chemicals has been studied using the so-called 'omics' technology of toxicogenomics, proteomics and metabonomics. Each technique has its strengths and weaknesses. The strengths of toxicogenomics (measuring the expression of thousands of genes at a time) are the large overview of a biological response perhaps finding unknown genes, and the relative sensitivity of the technique. Seeing patterns of changes may be more informative than changes in the expression of single genes but requires considerable bioinformatics expertise. Metabonomics (or metabolomics) uses NMR to produce profiles of tissue, serum or urine metabolites reflecting pathological states and drug induced toxicity. Metals often affect kidney function and thus are likely to change urine metabolite profiles.

Overview of use of 'Omics'



For humans, the greatest problem in using toxicogenomics is a source of cellular material. This is often restricted to the use of lymphocytes, semen, umbilical cord or biopsy specimens. However, in experimental exposures some toxicogenomic signatures are indicative of metal toxicity and if developed into PCR (polymerase chain reaction) methods they could be used as biomarkers for human exposure with small numbers of cells from lung gavage or saliva.

For instance, genomic response profiling of human lung cells in culture has enabled prediction of high and low dose exposures and distinguishing between metals such as Cd, Cr, Ni and As [Andrew *et al* (2003) *Environmental Health Perspectives*, **111,** 825]. It is important to stress that it is the gene expressions after exposure levels relevant to humans that are the most pertinent. At the relatively low doses of human occupational exposures this is challenging work. One toxic effect of arsenic in humans is thought to be linked to inflammation in atherosclerosis. By correlating exposure of humans to arsenic with expression of lymphocyte cytokines and growth factors associated with atherosclerosis, it has been possible to obtain some idea of the health risk to patients [Wu *et al.*, (2003) *Environmental Health Perspectives,* **111**, 1429].

In the future this kind of approach will be rewarding, but documenting well established exposures with good control groups will be of crucial importance to interpreting the results. Controlling for individual variability and types of metals or mixtures will be difficult problems. Eventually, how and by whom that information is stored and utilised will also be important issues.

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This article is an edited version of Dr Smith's talk at the ECG 2005 Distinguished Guest Lecture and Symposium. The two Environmental Health Perspectives *articles and the paper from the* Proceedings of the National Academy of Sciences USA *mentioned in this article may be downloaded for free from the Web.*

Meeting report

The 13th International Symposium of the Estuarine and Coastal Sciences Association

Estuaries and Coasts: The Ecosystem Approach

Sixty delegates attended this conference at Heriot-Watt University in September 2005, which was on the role of monitoring, modelling and management in achieving the Ecosystem Approach.

The symposium consisted of four sessions over three days, and some 35 papers and 12 posters were presented. The focus of the conference was on how ecosystem monitoring (the Ecosystem Approach) could be used as a means of assessing compliance with the Water Framework Directive and similar marine-linked protocols.*

The title of the opening address (Elliott, University of Hull), *The Ecosystem Approach: a unifying concept in a complex system - myth or reality*, reveals some of the uncertainties that exist for the likely success of such an approach as a pragmatic tool for estuarine management plans. Although the Ecosystem Approach is,

> *" . . . implicit or explicit in all recent marine management initiatives, including estuarine management plans . . . [which] includes, within Europe, the EC Water Framework Directive (WFD), the EC Habitats Directive, the EU Marine Strategy (and the proposed Marine Framework Directive) and the ICZM Directive, OSPAR Annex V, the EU Common Fisheries Policy ecosystem approach for fisheries, ICES ecosystem approach, strategic environmental assessment, FAO Ecosystem Approach to fisheries management etc."* (Elliott, *op. cit.)*

the work needed to:

- map and classify the various estuarine habitat zones
- identify indicator species (or species assemblages) for each of several zones in each estuary system
- obtain baseline values for these species, and
- monitor them (during a period of climate change) so that estuarine and coastal environmental quality can be assured

seems to be huge and difficult. Especially when the outcomes require local detail to be rounded-up through a series of crude parameterisations into simple classifications such as high, good, moderate, poor and bad.

Session One focused on macrobenthic communities and their use to study ecological status. O'Brien and co-workers (University of Melbourne) compared the effects of different nutrient sources on mudflat macrofauna in South Australia. The findings illustrate the difficulties relating to these studies. Small plots of sediment were dosed with either household garden fertilizer (Osmocote©) or, as a surrogate for a natural nutrient source, macroalgae (*Ulva* sp.). Although the concentrations of porewater nutrients (nitrate and phosphate) increased for the Osmocote©, this was not observed for the *Ulva* sp; and the observed outcome effects on higher trophic levels were inconsistent for both dosing regimes. The WFD defines nutrient thresholds (e.g. the High/Good threshold is 10.8 M DIN, the Good/Moderate is 22.7 M DIN) and, given the work presented above, it becomes important to make some assessment of whether these are intended to be universally valid thresholds with statutory implications or guidelines which have a locally interpretive range.

Under the sub-heading of Pollution, Judy Dobson (SEPA) spoke about the *Pressures and impacts on the Tay Estuary, Scotland*, including dumping, dredging, changes in morphology and marine discharges. The Tay is the biggest river in Scotland (100 $m^3 s^{-1}$ flow) and has high conservation value for over-wintering wading birds. Following upgrading of the Waste Water Treatment Works (WWTW) at Dundee and Perth, there have been significant improvements in water quality using a number of indicators: bacteriological, phytoplankton, heavy metals, macrofauna (fish) and physicochemical, e.g. dissolved oxygen, NH_4^+, NO_3^-. Newport and Tayport WWTWs will upgrade to tertiary treatment this year and further water quality improvements are expected with continuing monitoring to include macroalgae.

Session Two commenced with an overview of the WFD and the manner in which classification, monitoring and the consequent implementation of a 'Programme of Measures' (needed for at risk water bodies) will be put into practice. Aspects of this were illustrated by a paper by Wilkinson and co-workers (Heriot-Watt), *Using attached macroalgae to assess ecological quality of estuaries for the WFD*, which clearly demonstrated that the penetration of fucoids up an estuary could be used as a measure of improved environmental health. Brazier and co-workers (Countryside Council for Wales, Bangor) examined the use of angiosperms (seagrass) for a similar purpose (*Angiosperms within the EU WFD*),

> *"The WFD requires water bodies to be classified by their chemical and ecological status. The latter is principally a measure of the effects of human activities on water ecosystems. Of the biological parameters angiosperms are one of the quality elements used in defining the ecological status of a transitional or coastal water body. The attributes to be monitored include taxonomic composition and abundance. One of the key tasks in developing the classification systems for water bodies will be to identify appropriate reference conditions. Reference conditions are established from biological surveys and constitute an expectation of ecology found at reference sites i.e. those relatively undisturbed by anthropogenic activity. Calculating the extent of a quality element's deviation from reference conditions provides an ecological quality ratio used to classify water bodies."* (Brazier, *op. cit.*)

Other papers considered:

- the abundance and species composition of intertidal seaweed

communities for assessing the ecological quality of rocky seashores;
- the use of marine angiosperms for saltmarsh classification;
- the problems associated with “general physico-chemical’ quality elements” (taking into account the limiting effects on phytoplankton growth of turbidity, the non-linear relationship between biological changes and nutrient enrichment, and other confounding influences).

The final paper examined the Columbia River: *Classifying and characterizing landscape structure of complex tidal-freshwater to euhaline ecosystems in the Columbia River, USA* (Simenstad and co-workers, Seattle). This paper focused on the US system of ecosystem classification using remotely sensed data and *“statistically vigorous* in situ *monitoring to produce a spatial data-set classification that embraced ecotone transitions from tidal freshwater to euhaline ecosystems and which was able to capture change over time”.*

Session Three focused on modelling and mapping – in particular the use of MARGIS (which combines GIS with a numerical hydrodynamic and solute transport model to assess discharge consents in the EA’s NW region) and an estuarine hydrodynamic modelling system developed during the Suffolk Estuarine Strategies programme (Collings, Black & Veatch Ltd.). Phytoplankton indices as indicators of ecological health (especially eutrophication status) were also discussed.

The final session (**Session Four**) commenced with a paper entitled *Putting the ecosystem approach into practice – what do we need to do?* (Laffoley, EN), which encapsulated some of the difficulties to be overcome before the “Ecosystem Approach” achieves the utilitarian status necessary for environmental monitoring.

“There is however an ongoing debate about exactly how to implement it, and how it fits with and can improve the delivery of other high level principles like sustainable development. . . . From a scientific perspective adopting the Ecosystem Approach places new demands on the marine scientific community, in terms of the underlying science needed to promote recovery, sustainable use, and how some areas of existing work should now be augmented and developed e.g. ecosystem functioning. Improved mechanisms will be needed to ensure link-up between science, policy advisors and decision makers”. (Laffoley, *op. cit.*)

Other papers in this session described:

- salmon recovery in the Columbia River *(“. . . data underscore the importance of a whole-basin perspective to account for riverine-estuarine-marine habitat linkages and ensure the continuity of salmon life cycles.”*);
- the Irish Sea (the Irish Sea Pilot for Marine Spatial Planning which suggests zoning the Sea into four main categories: general use (GUZ), conservation priority (CPZ), exclusion (EZ) and protected (PZ));
- horizontal and vertical network relationships between Local Coastal Partnerships (the Tay Estuary Forum) and national bodies (the Scottish Coastal Forum).

I make three observations in relation to the substance of the conference:

1 Techniques for measuring nutrients (nitrogen and phosphorus in their various oxidation states) and dissolved oxygen need to be developed, which are cheap, robust, telemetric, continuous and capable of reflecting the bulk and micropore chemistry – and that graduates need to be available who are adept at using them.

2 Chemists need to work more closely with ecologists to make links between physico-chemical data and hydroecological phenomena.

3 Reductionist approaches to complex systems have rarely been able to comprehend the natural world they seek to describe. In this case the search for effective holistic descriptions is likely to detract from the robust application of the precautionary principle, provide spurious legitimacy to eco-unfriendly legalistic arguments, and ultimately be responsible for microscale degradation of the environment. In addition, the financial resources of the Environment Agency will be drained and attempts to strengthen environmental legislation during a period of population growth and climate change weakened.

[*] *The Ecosystem Approach: Coherent Actions for Marine and Coastal Environments*, English Nature 2004, Catalogue Code CORP1.68, www.english-nature.org.uk.

Estuarine & Coastal Sciences Association (ECSA) http://www.ecsa-coast.org/

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Meeting report

Monitoring Ambient Air 2005

In December 2005, the RSC's Automation and Analytical Measurement Group (AAMG) organised a two-day meeting, *Monitoring Ambient Air 2005: Diffusive Monitoring Techniques and Applications*, which was held at the English Heritage Lecture Theatre, London.

The first paper (Kobe, DG Environment, EC) in session one covered the generalities of the EC Ambient Air Directives (http://europa.eu.int/comm/environment/air/cafe/index.htm). Future actions include a revision of the National Emissions Ceiling Directive and the development of new standards for vehicles, for emissions from ships (NO_x), for agriculture (NH_3) and for $PM_{2.5}$ (notably because "…in 2020 approximately 270 000 EU citizens will die prematurely due to fine particles."). This paper was followed by *Diffusive sampling: what's new?* (Hafkenscheid, Delft) which considered recent (since 2001) standardization efforts (e.g. EN 13528, EN 14412, EN 14662) and also identified that the use of diffusion sampling for ambient (rather than indoor) air monitoring (NH_3, NO_2, O_3, SVOC) was increasing. The paper also discussed the future of SPMD (Semi-Permeable Membrane Devices) for diffusion sampling and ended with a call for more collaborative studies around diffusive sampling. During the question and answer session the problem of monitoring VOCs was raised, as VOCs can present in particulate (condensed) form. Hafkenscheid acknowledged the problem and pointed out that field studies and laboratory results had already proved to be markedly different.

The afternoon session commenced with a paper by Alan Braithwaite (Nottingham Trent University) *Principles and practice of diffusive monitoring and the application to ambient air pollution*. This discussed the background to diffusive processes (Boyle, Charles, Graham, Maxwell and Fick). The next paper (Ullrich, Federal Environment Agency, Berlin) was *A critical appraisal of monitoring techniques*, which examined the European standards for diffusive samplers (e.g. EN13528, EN 14412). It also discussed the associated validation campaigns (which occurred chiefly in relation to the EC Benzene Directive) from which it can be considered that "…the combined uncertainties of diffusive and pumped sampling were equal with values of about 10%." The paper pointed out a particularly critical feature of diffusive samplers viz. "…the strong dependence of the uptake rate on the velocity of the adjacent airflows". This begs the question, "…do weather shields have an effect on the air flow and velocity around passive diffusion tubes".

Papers on ozone and its precursors closed the day. These speakers suggested that there were circumstances under which diffusive samplers could contribute information which may have relevance to the larger studies of ozone formation.

The third session (Day 2) commenced with a paper *Which sorbents to use and when – a practical guide* from Elizabeth Woolfenden (Markes International Ltd., UK). It discussed the need for careful sorbent selection to achieve a quantitative and efficient release of the compounds of interest and focused on problems of impedance ('blocking') of tubes. The quantitative re-collection of material onto a clean sorbent tube after sampling and analysis acts as a good quality validation process re-sampling efficiency. Uwe Kuhn (Max Planck, Mainz) then talked about automated flow sampling for sequential sampling of VOCs – this was a paper based around the necessary design criteria for such instrumentation (e.g. the installation of different cartridges, the inclusion of ways for easily modifying sampling parameters, electronic storage of data as an audit trail, low cost, field portability and sufficient sampling loops to collect at least two samples (for QA)). The speaker illustrated the application of this device for measuring the natural contribution of VOCs to the atmosphere from vegetation.

Tang and co-workers (CEH, Edinburgh) spoke on NH_3 monitoring in the UK. Ammonia emissions are estimated to have doubled over the last century across Europe (increased N-fertilisers and farm animals). Legislation [UNECE Gothenburg 1999 (acidification and eutrophication); 2010 EC National Emissions Ceiling Directive; IPPC in relation to intensive pig and poultry farms] is available to support ammonia reduction and in the UK the 94 site National Ammonia Monitoring network (NAMN) (www.edinburgh.ceh.ac.uk/cara/) looks at the quantification of " . . . temporal and spatial changes in air concentrations and deposition of gaseous NH_3 and aerosol NH_4^+ on a long term basis" using both passive and active diffuse samplers. The monitoring network provides valuable background data against which the success of attempts made to reduce UK ammonia emissions can be measured.

The fourth paper in the third session was *New applications for diffusion samples* (Martin Ferm, Gothenburg). This focused on the measurement of atmospheric HNO_3 concentrations "… passive long-term integrative techniques" (i.e. tubes). The tubes are small, lightweight, have no power requirements, are noiseless, measure in situ, and are technically easy to use. The speaker pointed out that such methods are particularly appropriate for measuring external and internal effects (corrosion) on (and in) historic buildings.

The final session of the conference started with a paper from Brian Goody (NPL) *A controlled atmosphere test facility for traceable measurement of uptake rate with variable uncertainties*. The NPL facility " … is designed to test and calibrate field samplers over wide ranges of ambient temperature, humidity and air speed." And is "…available to manufacturers and users of diffuse samplers to determine uptake rates in selectable ambient conditions and atmospheres". This was followed by a paper which discussed the maintenance of a Local Air Quality Management website which used (amongst other data) information from diffusion tubes (Monica Price, Sunderland).

The penultimate paper (*Use of diffusive samples to determine air quality and ventilation* Crump, BRE) discussed indoor air quality and the growing recognition of its significance in estimating the damage to human health from exposure to air of poor quality. Diffusive samplers have several advantages as monitoring devices for indoor air quality e.g. long-term, minimal disturbance etc. The final paper (Tipler, Perkin Elmer, USA) was *Methodology for assessing the packing integrity of absorbents within thermal desorption tubes and traps*. Voids in tube packing material (caused by settlement or contraction of the packing) can have severely deleterious effects on data due to channelling of the gas flow during pumping and desorption. The speaker advised that the condition of the packing be assessed visually (glass tubes) or by measuring the pressure drop across opaque tubes (by adapting technology available on modern desorption instrumentation to perform an automated measurement of packing impedance.

Several posters were displayed (including Barnes, Ledbrooke and Parsons *Nitrogen dioxide diffusion tube 'cluster' surveying – a transport planning tool*). A magnum of champagne (donated by Markes International Ltd) was won by Jo Barnes (Cornwall College Air Quality Unit).

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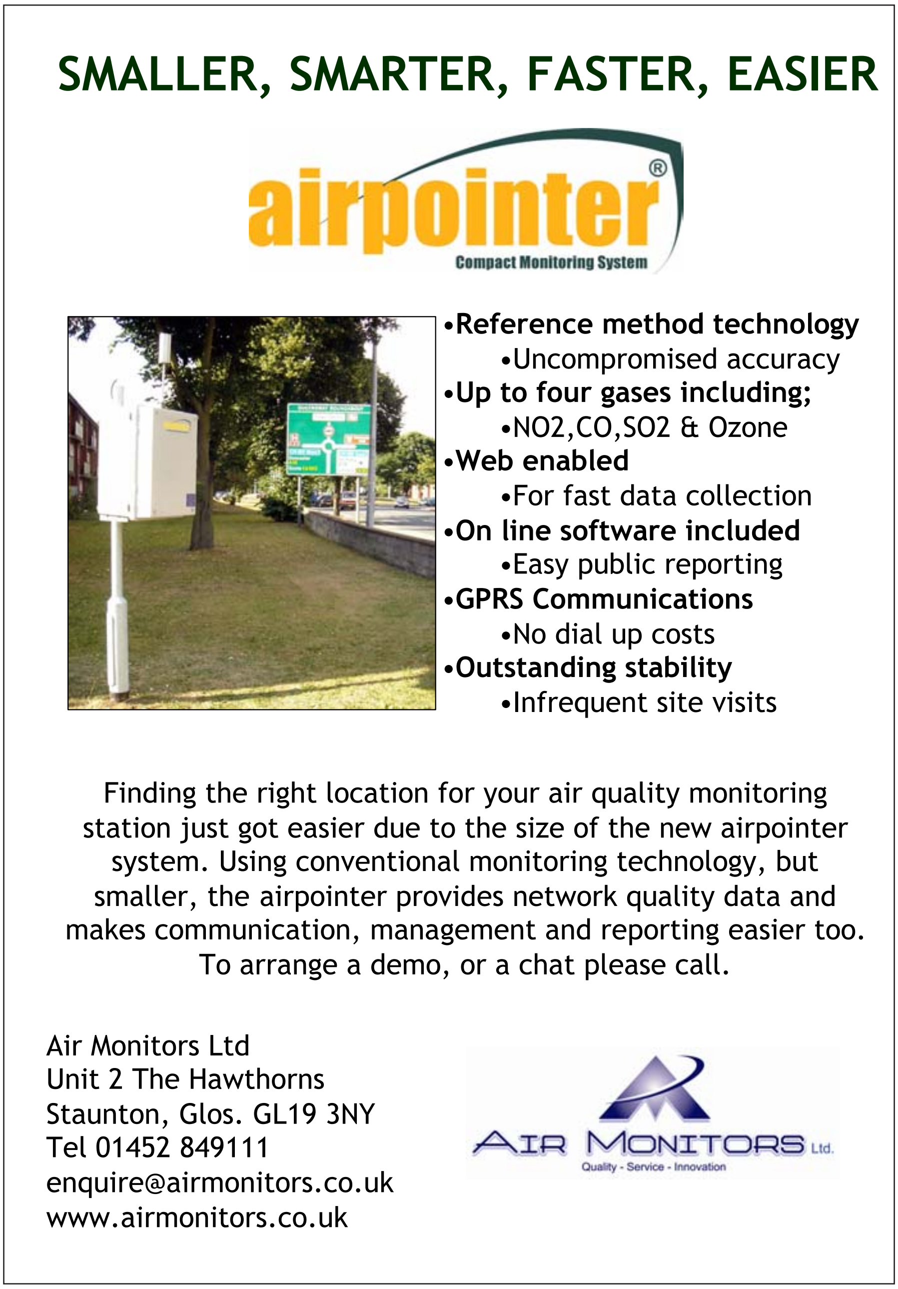

Recent books on the environment and on toxicology at the RSC library

The following books and monographs on environmental topics, toxicology, and health and safety have been acquired by the Royal Society of Chemistry library, Burlington House, during the period June to December 2005.

Aquatic Hazard Assessment II
(ECETOC Technical Report No. 91)
ECETOC, Brussels, 2003

Fume Cupboards: Part 1 Vocabulary
British Standards Institution, Milton Keynes, 2003

Fume Cupboards: Part 2 Safety and Performance Requirements
British Standards Institution, Milton Keynes, 2003

Hair in Toxicology: An Important Biomonitor
(Issues in Toxicology)
D. J. Tobin (ed.)
Royal Society of Chemistry, Cambridge, 2005
ISBN/ISSN: 0854045872

Nanotechnology and the Environment: Applications and Implications
(ACS Symposium Series No. 890)
Karn, B. *et al* (eds.), Oxford University Press Inc, USA
ISBN 0841238774

Persistence of Chemicals in the Environment
(ECETOC Technical Report No. 90)
ECETOC, Brussels, 2003

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