



January 2006

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Arsenic in the air ..... 2  
Arsenic contamination in  
Bangladesh and northern India: an  
update

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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%

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 ( $\text{As}_4\text{S}_4$ ), orpiment ( $\text{As}_2\text{S}_3$ ) 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 ( $\text{CuAs}_2\text{O}_4$ ) and cupric acetoarsenite [ $\text{Cu}_4(\text{OAc})_2(\text{AsO}_2)_6$ ]. 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 ( $\text{AsO}_4^{3-}$ ) under

oxidized conditions, or trivalent arsenite [ $\text{As}(\text{OH})_3$ ] under anaerobic conditions.

Sediments that are carried down by the vast network of rivers draining the Himalayas most its th 1 Tc-0.7 TAs.2Pigment93rbi

dissolved from the  $\text{FeO}(\text{OH})$ , this leads

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,  $\text{H}_3\text{AsO}_3$ ,  $\text{p}K_a$  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.



# 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  $\text{As}(\text{OH})_3$  and arsenate  $\text{AsO}(\text{OH})_3$ , has a high acute toxicity. By contrast arsenobetaine  $(\text{CH}_3)_3\text{As}^+\text{CH}$

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  $^{40}\text{Ar}^{35}\text{Cl}^+$  can interfere, and its formation has to be monitored by other mass/charge channels e.g.  $m/z$  77

( $^{40}\text{Ar}^{37}\text{Cl}^+$ ). 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.

This combined MS technique has been

mainly to ribose derivatives as arsenosugars.

Although arsenic is known to accumulate in seaweed naturally, these macroalgae are still widely used as cqcqcqcqcqcqcqcqvry and

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?

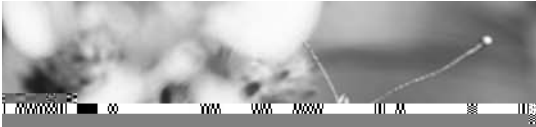
**Phytochelatins.** Larger labile complexes of arsenic with polypeptides may be formed in the plants. In particular, cysteine-rich phytochelatins (PCs) are thought to influence the tolerance of the plants towards metals and their ability to accumulate and translocate arsenic from the roots into leaves 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





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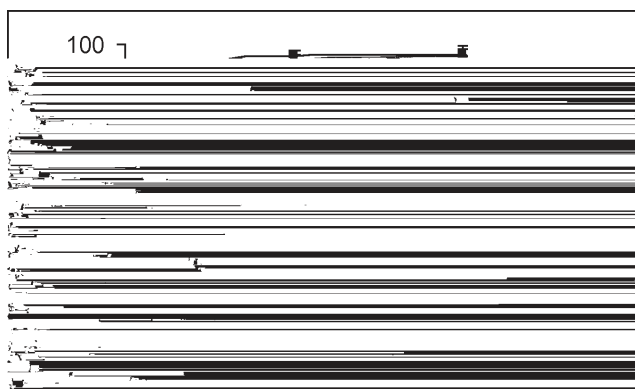
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## The use of dried hyacinth roots to remove arsenic from surface water

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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



**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  $200 \mu g As l^{-1}$  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



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

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].

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 pE) 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.

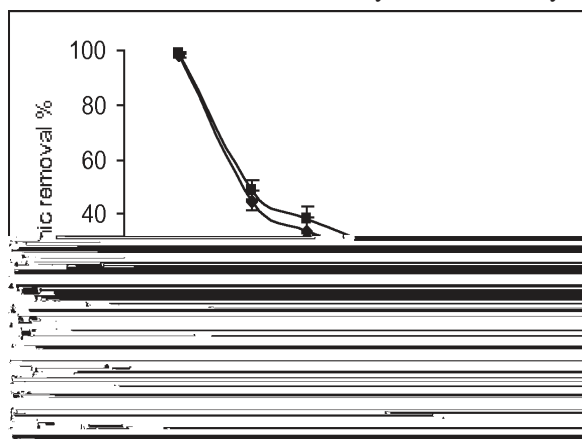
The need for materials to remove arsenic from waters used for drinking and irrigation of crops has been recognized for a number of years and many different materials

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  $10 \mu g$  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  $1500 \mu g As l^{-1}$  (Figure 4) removed up to  $50 \mu g As g^{-1}$  of roots. Assuming an arsenic solution concentration of  $1500 mg l^{-1}$ , approximately 30 grams of dried roots would be required to remove  $1500 \mu g$  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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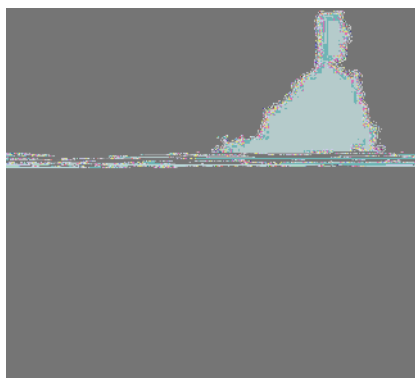


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## Monitoring of ambient air particulate arsenic concentrations at nine sites in Cornwall

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



**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  $0.08 - 2.78 \text{ ng m}^{-3}$ . 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 ( $1 - 4 \text{ ng m}^{-3}$ ) (Maggs 2000). Most concentrations are below this range and all are well below the EU Air Quality guidelines of  $6 \text{ ng m}^{-3}$  (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



**Figure 3**



**Figure 2**

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  $\text{PM}_{10}$ -arsenic in Cornwall.

### 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 ( $0.5 \mu\text{m}$ ) 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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Professor Peter Liss (2002), and Professor Jane Plant (2005).

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

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## Uranium in UK stream sediments, soils and stream waters

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  $^{238}/^{235}\text{U}$  ratio being constant, with the single exception of the very ancient natural reactor at Oklo in Gabon; whilst the range of the  $^{238}/^{234}\text{U}$  ratio is affected by leaching processes, preferentially removing  $^{234}\text{U}$  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  $^{238}/^{235}\text{U}$  ratio, as this is virtually constant in nature. The incorporation of fuel cycle uranium wastes into the environment results in the superimposition of anthropogenic  $^{238}/^{234}\text{U}$  on the natural  $^{238}/^{234}\text{U}$  variation, making

source apportionment more difficult than using  $^{238}/^{235}\text{U}$ .

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

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 from 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

# 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

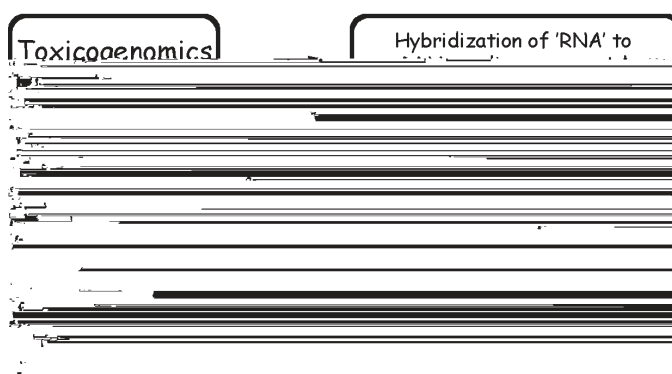
Over recent years the complexity of experimental response to drugs and chemicals has been studied using the so-called 'omics' technology of toxicogenomics, proteomics and

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.

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

## 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

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 13<sup>th</sup> 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 papersagtonsistedagtosity io sistedystem

- 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<sup>3</sup> s<sup>-1</sup> flow) and has high conservation value for overwintering 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<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>. 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;
-

## Meeting report

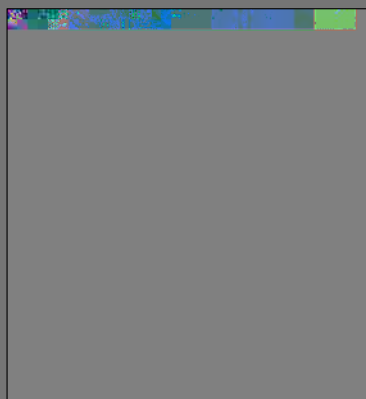
examined the European standards for diffusive samplers (e.g. EN13528, EN 14412). It also discussed the associated validation campaigns (which occurred chiefly in relation to the EC Benzene Directive) from which it can be considered that "...the combined

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).

**ALEX LEDBROOKE & 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

## **Environmental Biology for Engineers and Scientists**

DAVID A. VACCARI, PETER F. STROM, JAMES E. ALLEMAN

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