Bulletin

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Posters from the 22nd European Meeting of the Society for Environmental Geochemistry and Health

The 22nd European Meeting of the Society for Environmental Geochemistry and Health (SEGH) was held in April 2004 at the University of Sussex. Arsenic contamination and remediation were the topics for many of the papers and posters at this meeting, and we are grateful to **Professor Mike Ramsey** from the Centre for Environmental Research at the University of Sussex for permission to reproduce the following posters, which relate to current concerns over arsenic contamination.

MECHANISMS INVOLVED IN BIOLEACHING OF ARSENIC IN TAILINGS BY ISOLATED BACTERIUM

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Arsenic exerts toxic effects to wildlife and human health. Especially tailings which are by-products from mining and smelting activities, without appropriate treatment, can serve as point sources of As contamination to nearby soil, sediment, and aqueous systems. Biological treatment using microorganisms can be applied to remove or reduce As from the tailings in an efficient and cost-effective way. Some species of microorganisms are reported to alter the valence state of As. Because reduced form of As, As(III), is more mobile than As(V) in natural settings, microbial change of the chemical species of As can play important roles in enhancing transportation and mobilization of As from solid matrix. In addition, microbial mediation of Fe can also significantly affect the fate of As since Fe-oxides are considered to be responsible for As sorption and immobilization. The main mechanisms related with the enhancement of As mobility can be summarized as: 1) reductive dissolution of Fe-oxides by Fe-reducing bacteria and 2) direct As reduction by dissimilatory reduction or detoxification mechanism. The objectives of this study were to investigate the behaviour of As in the tailings by microbial activity and to elucidate the potential of As bioleaching process using indigenous bacteria to remediate As-contaminated tailings.

Total and sequential extraction results showed that 78% of total As (3,200 mg/kg) occurred as Fe-oxide-associated phase in the studied tailings from an abandoned Au mine. In bioleaching tests, indigenous bacteria isolated from the tailings were added and incubated in 5 mM glucose solution (295 mL) with the tailings (9 g) in flasks. Abiotic controls were included in the experimental set to compare the result. The supernatants from the flasks were periodically collected and pH, total As, and Fe^{2+} concentrations were measured. After bioleaching tests, variation in mode of As occurrence in the tailings was determined by sequential extraction technique.

Extracted amounts of total As and Fe^{2+} from the tailings increased until 12 days and then were maintained constantly. Sequential extraction analysis of the tailings after bioleaching tests showed that Fe-oxide-associated phase decreased by 40%, which indicated that dissolution of Fe-oxides by microbial activity increased the mobility of As. Maintenance of the amount of dissolved As after 12 days indicated that a steady state might occur between dissolution and reprecipitation of Fe-oxides rather than the cessation of microbial activity. In a continuously flowing system, the extent of microbial As leaching was much greater than that of the batch systems.

ARSENIC-HYPERACCUMULATOR SCREENING TEST AND ITS ELEMENTS DISTRIBUTION

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Several fern species were screened by their tolerability and uptake of arsenic. The test plants were classified into 4 groups according to tolerability and accumulation efficiency of arsenic. Arsenic and other elements in the fronds and roots of the plants were determined by Inductively Coupled Plasma (ICP) spectrometry. *Pteris cretica* var. *albolineata* was chosen as an arsenic tolerant and hyperaccumulator fern while *Microlepia strigosa* was chosen as an arsenic sensitive fern. The arsenic tolerability of *Pteris cretica* was 14 times higher than that of *M. strigosa*. The 28 day EC-50 of both fern species was 9.32 and 0.66 mg L^{-1}, respectively. The longer the exposure times the higher the toxicity of arsenate to ferns. *P. cretica* contained a very high arsenic level in the frond, i.e., 2,200 µg g^{-1}, while the arsenic concentration in the root was 640 µg g^{-1}. The translocation factor of *P. cretica* and *M. strigosa* were 3.28 and 0.44, respectively.

The elements concentration and localisation was confirmed by Particle Induced X-ray Emission Spectroscopy, PIXE (Ryan, 1990). The concentrations in the frond and root tissues measured by PIXE were in close agreement with ICP spectroscopy. The average arsenic concentrations measured by PIXE were slightly higher than those determined by ICP spectroscopy. Mapping of arsenic in the exposed *P. cretica* showed significant variation between the base and the apex of the frond. Arsenic and calcium had higher concentrations at the apex than at the base. This behaviour was opposite in

phosphorus and potassium. The highest arsenic concentration was found at the tip and around the apex area a concentration as high as 1.05% or 10,500 µg g^{-1} was recorded. In some parts of the root, arsenic concentration was found as high as 0.5%. The part of the root that showed very high As concentrations also showed high concentrations of iron up to 0.46%. The iron and As concentrations were in good correlation in the root but not in the frond.

Reference

Ryan C.G., Cousins D.R., Sie S.H., Griffin W.L, 1990, *Nuclear Instruments and Methods in Physics Research*, **B49**: 271.

REMEDIATION OF ARSENIC AND COPPER CONTAMINATED SITE IN SW ENGLAND – INITIAL INVESTIGATIONS

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Leaching of arsenic from soil creates a great potential hazard for groundwater contamination. Treatment of arsenic rich soils, particularly when arsenic is accompanied by other potentially toxic metals, such as Cu, presents a particular challenge due to contrasting behaviour of the two elements.

An As and Cu contaminated old mining site in SW England is being studied. The aim of the project is to investigate 1) the distribution and speciation patterns of the two contaminants; 2) possible remediation options with emphasis on metal/arsenic immobilization in soil and revegetation and 3) the fate of both elements in soil given remediation options recommended and/or possible future management scenarios.

Total metal and arsenic content were measured by ICP-AES in soils following $HNO_3/HCLO_4$ digest and in plants following HNO_3/H_2O_2 digest. ED SEM and X-ray diffraction analyses were undertaken on soil samples. Fractionation of As and Cu in soil was further studied by sequential extractions. Initial leaching experiments have been conducted on the waste tip material.

The mean As content in waste material is 17000mg/kg, while copper-1750mg/kg. The soil is very acidic (pH<4) and with low OM content (3%). *Calluna vulgaris* is a dominating species colonising the site. This plant appears to operate exclusion strategy towards both As and Cu as indicated by very low Bioaccumulation Coefficients (BAC): 0.004 for As and 0.012 Cu. The As content of the plant ranged 2.5- 360mg/kg, while Cu: 4.3-89mg/kg.

Natural immobilization of As appears at some parts of the site, where As is found to be fixed in a form of iron arsenates and iron-lead arsenates. Primary As and Cu minerals– arsenopyrite and chalcopyrite were found in samples from the waste tip.

Only 0.002% of total arsenic was leached out by 0.01M $CaCl_2$ as compared to 3.25% of total copper being solubilised in the same conditions. The fate of both As and Cu can be

influenced significantly by adding organic matter and phosphorus which were found to stabilise Cu but mobilise As in the waste material.

Due to low pH and low OM content treatments such as liming and compost additions could be beneficial, but may potentially increase As mobility. This and other treatments aiming for copper stabilization will be now further tested in leaching columns. Possible influence of revegetation will also be studied.

ARSENIC IN SOUTH WEST BRITAIN

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The south-western peninsula of England is extensively contaminated with heavy metals arising from centuries of mining activity in the region. From about 1860 to 1900, this region was the world's major producer of arsenic. Mining and smelting activities have left a legacy of contaminated land, with As and Cu rich mine tailings. One of the largest As-Cu mines (Devon Great Consols, and the nearby village of Gunnislake) lies in the valley of the River Tamar, a natural boundary between the counties of Devon and Cornwall. This area has large areas of soil rich in As and Cu. Further extensive areas of land were contaminated with fallout from the smelting process and it is estimated the in Devon and Cornwall some 700 km^2 of land are affected. Most of the contaminated area is agricultural with villages and small towns; urban development has sometimes taken place on contaminated land

The aims of this research are to estimate human exposure from arsenic contaminated soils and dusts, by means of environmental measurements and the determination of arsenic metabolites in the urine of residents, and finally to use Risk Assessment protocols to assess potential risk. This poster reviews the studies on arsenic in the Tamar Valley in southwest England by the Environmental Geochemistry Research Group at Imperial College. These include a geochemical survey of the area, determination of arsenic metabolites in urine of local residents (1), Risk Assessment using the CLEA model, and mineral speciation of arsenic in soil particles together with arsenic solubility.

(1) Kavagnah, P., Farago, M.E., Thornton, I., Goessler, W,. Kuehnelt, D., Schlagenhaufen, C., Irgolic, K.J. 1998. Urinary arsenic species in Devon and Cornwall residents, UK, *Analyst*, **123**, 27.

NATURAL ORGANIC MATTER IN SEDIMENTARY BASINS AND ITS RELATION TO ARSENIC IN ANOXIC GROUND WATER: THE EXAMPLE OF WEST BENGAL AND ITS WORLDWIDE IMPLICATIONS

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Ground water worldwide is at risk from natural As pollution. In the Ganges Plain, 25% of ground-water wells contain $> 50\ \mu g\ l^{-1}$ of As, the consumption of which threatens the health of millions of people. In order to show how the As gets into the water, we sampled ground waters from piezometer nests and wells, and sediments, from a field site at Barasat, West Bengal. Concentrations of As reach $1180\ \mu g\ l^{-1}$ and are accompanied by concentrations of Fe up to $13.7\ mg\ l^{-1}$. Ground water that is rich in Mn ($1 - 5.3\ mg\ l^{-1}$) contains $< 50\ \mu g\ l^{-1}$ of As. The composition of shallow ground water varies at the 100m-scale laterally and the metre-scale vertically, with vertical gradients in As concentration reaching $200\ \mu g\ l^{-1}\ m^{-1}$. The As is supplied by reductive dissolution of FeOOH and release of the sorbed As to solution. The process is driven by natural organic matter in peaty strata both within the aquifer sands and in the overlying confining unit. In well waters, thermo-tolerant coliforms, a proxy for faecal contamination, are not present in high numbers (< 10 cfu/100 ml in 85% of wells) showing that faecally-derived organic matter does not enter the aquifer nor drive reduction of FeOOH, and so does not contribute to As pollution. Reduction of FeOOH is not driven by surface organic matter, from river beds, ponds, and soils, that is drawn into the aquifer by irrigation drawdown, as has been proposed by Harvey *et al.* (2002) in a model that seeks to re-link irrigation and high concentrations of As in ground water. Should such a re-linking lead to renewed calls to curb irrigation with ground water, the livelihoods of the rural poor will be affected adversely.

Arsenic concentrations are high ($>> 50\ \mu g\ l^{-1}$) where reduction of FeOOH oxide is complete and its entire load of sorbed arsenic is released to solution, at which point the aquifer sediments become grey in colour as FeOOH vanishes. Where reduction is incomplete, the sediments are brown in colour and resorption of arsenic to residual FeOOH keeps arsenic concentrations below $10\ \mu g\ l^{-1}$ in the presence of dissolved iron. Sorbed arsenic released by reduction of manganese oxides does not release arsenic to ground water because the arsenic resorbs to FeOOH. High concentrations of arsenic in alluvial aquifers of the Bengal Basin arises because Himalayan erosion supplies immature sediments, with low surface-loadings of FeOOH on mineral grains, to a depositional

environment that is rich in organic mater so that complete reduction of FeOOH is common.

Harvey C.F., Swartz C.H., Badruzzaman A.B.M., Keon-Blute N., Yu W, Ali M.A., Jay J., Beckie R., Niedan V., Brabander D., Oates P.M., Ashfaque K.N., Islam S., Hemond H.F. and Ahmed M.F. 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science*, **298**, 1602 –1606.

ARSENIC AND HEAVY METAL IMPACT IN MINING AND INDUSTRIAL ENVIRONMENTS FROM SOUTH SCOTLAND AND NORTH WEST ITALY

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This investigation focuses on a former antimony mining and smelting site (Glendinning, S Scotland) and an area in NW Italy (Pieve Vergonte, Piemonte), affected by industrial activities superimposed on a region where historical contamination arises from Ag/Au mining. Levels of arsenic and heavy metals, which could be potentially harmful, were found to be high across large areas of the sites. Using these locations as test sites, this study investigates the potential for different biological indicators (e.g. ferns, sheep faeces) and other meaningful tools to identify spatial distribution of arsenic and heavy metals (Cu, Fe, Pb, Zn) in soil systems contaminated by a mixture of dumping, groundwater leaching and aerial deposition. Techniques such as ICP-AES and ICP-MS were used for determination of arsenic concentrations, SEM-EDS and XRD for physical characterization of arsenic pollution, and a five step sequential extraction (Wenzel, 2001) to identify arsenic distribution.

Results are presented from the first year of a 3-year PhD programme jointly between the University of Paisley and the University of Turin, and supported by the British Geological Survey (BGS, Keyworth) and the Italian Regional Environmental Protection Agency (ARPA, Piemonte).

The arsenic concentration in the soils from the mining site ranged from 99 to 19,367 mg/kg while for the soils from the Italian site these ranges where much lower, from 16 to 618 mg/kg. The highest bioconcentration factor (BCF) for arsenic was found in the sheep faeces (0.009). The mean factors for fern and sheep faeces in case of copper were 0.43 and 0.32 respectively. BCFs for lead and zinc were much higher in sheep faeces (0.036; 1.45) than in fern (0.007; 0.34). No crystalline arsenic phases were detected by XRD analysis. SEM-EDS observations of soil samples indicated mostly arsenic/iron association. The results of the sequential extraction show that the majority of arsenic (up to 60%) was leached during the third step, which dissolves amorphous and crystalline hydrous oxides of Fe and Al.

The correlation between soil samples and biota was linear and significant especially in case of Cu and Zn. The results obtained established fern and sheep faeces as suitable objects for further long-term monitoring research on these sites, which can provide quantitative information on different pollutions in soils.

Further work will focus on the application of the biomonitoring method in parallel with chemical techniques to extend the evaluation of contaminant dispersal and their wider environmental impact.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., and Adriano, D. C. (2001), *Analytica Chimica Acta*, **436**, p.309.

EXPOSURE AND RISK ASSESSMENT OF ARSENIC AND HEAVY METALS IN ABANDONED HWACHEON AND DOGOK MINE AREAS, KOREA

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In order to estimate the post-ingestion bioavailability of heavy metals and to assess the risk of adverse health effects on human exposure to toxic heavy metals, environmental geochemical surveys were undertaken around the Dogok Au-Ag-Cu and the Hwacheon Au-Ag-Pb-Zn mine sites. Human risk assessment of toxic heavy metals was performed with the results of the SBET (simple bioavailability extraction test) analysis for soil and chemical analytical data for crop plant and water.

Arsenic and other heavy metals were highly elevated in tailings from the Dogok (218 As mg/kg, 90.2 Cd mg/kg, 3,053 Cu mg/kg, 9,473 Pb mg/kg, 14,500 Zn mg/kg) and the Hwacheon (72 As mg/kg, 12.4 Cd mg/kg, 578 Pb mg/kg, 1,304 Zn mg/kg) mines. These significant concentrations can impact on soils and waters around the tailing dumps. The quantities of As, Cd and Zn extracted from paddy soils in the Hwacheon mine using the SBET analysis were 55.4%, 20.8% and 26.4% bioavailability, respectively, and for farmland soils in the Dogok mine, 40.8%, 37.6% and 33.0% bioavailability, respectively. Risk assessment modelling is subdivided into main four stages, i.e. hazard identification, exposure assessment, toxicity (dose-response) assessment and risk characterisation. In order to assess exposure it is necessary to calculate the average daily dose (ADD) of contaminant via the three identified pathways (soil, groundwater and food (rice grain) pathways). In dose-response assessment for non-carcinogens, reference doses (RfD) are calculated and that for carcinogens, slope factors (SF) are obtained by US-EPA *IRIS* database. In risk characterization, the results of toxicity assessment and exposure assessment are integrated to arrive at quantitative estimates of cancer risks and hazard quotients. Toxic risks are indicated in terms of a hazard quotient (H.Q.). H.Q. is ADD/RfD. The toxic risk exists for H.Q.>1. To arrive at the hazard index (H.I.) the ADD from three identified pathways (soil, groundwater and rice grain pathways) compared to the relevant RfD obtained from the *IRIS* database is summed. From the results of human risk assessment, HI (Hazard Index) value exceeded 1.0 for As in the Hwacheon mine and for Cd in the Dogok mine. Thus, toxic risks for As and Cd exist via exposure (ingestion) of contaminated soil, water and rice grain in these mine sites. The cancer risk for As by the consumption of rice and groundwater in the Hwacheon mine area was 8*E*-4 and 1*E*-4,

respectively. This risk level exceeded the acceptable risk (1 in 100,000) for regulatory purpose. Therefore, regular ingestion of local grown rice and groundwater by the local population can pose a potential health threat due to long-term arsenic exposure.

GEOCHEMICAL BEHAVIOR OF ARSENIC IN WATER SYSTEM AROUND THE ABANDONED MINES, KOREA

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Mining is one of the most important anthropogenically-induced sources of heavy metals in the environment owing to various mining activities. Especially, inorganic As is classified as human carcinogen and causes serious environmental problems in abandoned gold mine areas. Arsenic-containing minerals are common in gold-bearing rocks and gold mining has been associated with release of high levels of As into the environment. The objectives of this study are (1) to investigate the extent and degree of As contamination in water system; (2) to identify As species in surface and groundwater to assess environmental toxicity; (3) to examine chemical form of As in sediments using sequential extraction analysis. Mine, stream and groundwater samples were collected around the Dongil, the Okdong, the Dongjung, the Hwacheon, the Songcheon, the Dogok and the Gubong Au-Ag mines which are all fissure filling deposit and major metallic minerals of gold-silver, although the Okdong mine is typical base metal mine, the exploitation of gold-silver was reported. Physical properties such as pH, Eh and Conductivity were measured in the field. Water samples were also analyzed for cations by ICP-AES and for anions by IC. Arsenic speciation was carried out using silica-based anion exchange cartridges and their concentration was measured by hydride generation-AAS. The series of extractants used for As in sequential extraction analysis have been investigated by some researchers due to particular chemical properties of As, a metalloid and anions in environmental media. In this study, modified sequential extraction procedure using various extractants ($MgCl_2$, NaH_2PO_4, NaOAc, $(NH_4)_2C_2O_4$, $H_2C_2O_4$ and aqua regia) was adopted for determining chemical form of As in sediments. Highly elevated level of As was determined in mine water from the Dongil (524 µ/L) and the Dogok (56 µ/L) mines, and in stream waters from the Dongil, the Songcheon and the Gubong mine areas with the range of 63.7~117.6 µ/L, 6.7~764.3 µ/L and 56.1~62.9 µ/L, respectively. Arsenic concentration of groundwater, which is currently used for drinking water in he Okdong, the Dongil and the Songcheon mine areas, was higher than the permissible level(50 µ/L) of drinking water standard in Korea. The concentration ratios of As (III) to As (total) show the ranges of 46~95% in stream waters and 39~82% in groundwaters. As (III) ratio increases at the neutral pH (7~8) and low Eh condition. From the sequential extraction analysis of stream sediments, coprecipitated As with amorphous Fe oxyhydroxides was predominant with 21.7~40.5%. This indicates that severe contamination of As could occur by re-extracting under the reductive environment.