

The effects of organics on the transformation and release of arsenic

W.M. Al Lawati, B.E. van Dongen & D. Polya

School of Earth, Atmospheric and Environmental Sciences, Williamson Research Center for Molecular Environmental Science, The University of Manchester, Manchester, UK

Jiin-Shuh Jean

Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan

Thomas R. Kulp

Department of Geological Sciences and Environmental Studies, Binghamton University, NY, USA

Michael Berg

Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

ABSTRACT: Over a hundred million people across the globe are chronically exposed to high levels of Arsenic (As) in shallow reducing groundwaters utilized for drinking, cooking and irrigation. The importance of the role of degradable organic matter (OM) is widely recognized in As mobilization by microbially mediated reductive dissolution of iron (Fe-III) hydrated oxides/hydroxides and/or reduction of As(V). However, the role that organics play in As release in high-As aquifers remains ambiguous in many regions. Initial results of the organic analysis of the hydrocarbon fractions of sediments obtained from SW Taiwa (Yichu) and the Red River Delta, Vietnam (Van Phuc Village) revealed an influx of mature OM source in these sediments. The mechanism and the controlling factors on the release of As from these sediments are investigated.

1 INTRODUCTION

Millions of people worldwide are exposed to elevated levels of Arsenic (As) in the water they consume (Ravenscroft et al. 2009) and thousands are dying annually as a result (Polya et al., 2010). Arsenic is released from rocks and sediments into groundwaters, by both natural processes and anthropogenic activities. However, arguably the most widely accepted mechanism of As release into shallow groundwaters in As hot spots in West Bengal and Bangladesh, Cambodia and Vietnam is via microbially mediated reductive dissolution of As-bearing iron oxyhydroxides and/or derived by dissimilatory As(V) reduction (Islam et al. 2004, Polya et al. 2005, 2010, Berg et al. 2008). Recent studies suggest that the overall controlling factor driving the release of As in shallow reducing groundwaters is the reactivity of the OM present (Postma et al. 2007). However, Gault et al. (2005) has shown that it is not the total amount of OM that controls As mobilisation. Indeed, Héry et al. (2010) has found that As may be mobilised even from very organic lean sediments. It remains to be seen if the OM composition in high As shallow

aquifers are comparable to those already investigated in Cambodia (van Dongen et al. 2008) and West Bengal (Rowland et al. 2006).

Here, two sets of sediments from other As hot spot areas, Yichu (N 23.25, E 120.25) in Taiwan and Van Phuc village (site L; N 105.89, E 20.92 and site H; N 105.89, E 20.91) in Vietnam (Berg et al. 2008, Al Lawati et al., 2012), were chosen for OM characterization. These were then correlated to the amount of As in the aquifers and microbial communities present (Vietnam sediments) or to the rate of As(V) reduction and subsequent release of As(III) in pore waters of microcosm slurry incubations (Taiwan sediments).

2 SAMPLE SITES

2.1 *Sample collection from Taiwan*

Sediments were obtained from Yichu, an As hot spot in SW of Taiwan. Two sets of samples were obtained: first set (from 3–17.8 m depth; aerobic conditions; stored at –20°C) and second set (from 17.8–200 m depth; anaerobic conditions;

stored at 4°C). Solid phase As ranged from 0.8 to 23 mg/kg.

2.2 Sample collection from Vietnam

Sediments were obtained from Van Phuc village, on the Red River Delta, northern Vietnam, from two sites: first site (Holocene age; high groundwater As (Site H) up to 600 [g/L) and second one (site L) (Pleistocene; low groundwater As less than 10 [g/L). Solid phase As ranged from 2 to 29 and from 1 to 30 mg/kg at site L and H, respectively.

3 RESULTS AND DISCUSSION

A total of 13 sediment samples from Taiwan and from Vietnam were analysed for the composition of the hydrocarbon fraction (some results are shown in Table 1). All hydrocarbon fractions from the study sites showed general predominance of High Molecular Weight (HMW) *n*-alkanes (C₂₀–C₃₄). The carbon preference index (CPI) values, the Average Chain Length (ACL) and the abundance of an *n*-alkane were used to assess the sources of *n*-alkanes. These results, in combination with the abundant levels of the hopanes and the presence of unresolved complex mixtures, reveal lipid biomar-

Table 1. Total high molecular weight *n*-alkane abundance and ratios of OM in sediments from Yichu, Taiwan (7 samples) and Van Phuc village, Vietnam (6 samples).

Sample	Depth/m	<i>n</i> -alkane ^a	CPI ^b	ACL ^c	C _{max} ^d
<i>Taiwan</i>					
Oxic	12	720	1.9	27	31
Oxic	17.3	1800	1.0	23	20
Anoxic	17.8	350	1.2	24	21
Anoxic	40	1100	1.3	25	21
Anoxic	65	480	1.2	23	21
Anoxic	80	520	1.8	28	29
Anoxic	100	21	1.1	24	22
<i>Vietnam-site L</i>					
L0580	5.6	360	3.6	28.8	31
L0990	12	521	3.3	29.4	29
L14100	19.7	63	1.3	26.8	31
<i>Vietnam-site H</i>					
H2450	27.4	198	1.1	23.2	20
H3055	34.8	47	1.2	22.7	20
H3605	45	83	1.3	24.3	20

^aThe sum of concentrations (*n*-alkanes, C₂₀–C₃₄), ng/g sediment; ^bCPI = carbon preference index over the range C₂₀–C₃₄; ^cAverage chain length of the alkanes present; ^dChain length of the alkane chain with highest concentration.

kers of predominantly terrestrial origin with an influx of petroleum-derived OM source.

Microcosm experiments using sediment slurries from Taiwan, indicated that As release is a microbial process however, no correlation was found between the total As release and the different types of OM analysed (e.g. TOC, *n*-alkanes, *n*-alanoic acids, *n*-alkanols), suggesting that (i) part of the OM that was considered to be less bio-available could still be degraded/used as electron donor or (ii) other electron donors, not analysed in present study could be contributing/controlling the rate of As release.

Organic geochemical combined with microbial analyses of the sediments from Vietnam suggested that (i) groundwater As concentrations at both the low As and high As sites are not caused by *in situ* microbially mediated reductive transformations of As-containing iron (Fe-III) oxides and that (ii) these processes are not critically limited by the absence of OM electron donors or solid phase sedimentary As.

4 CONCLUSIONS

- Organic geochemical analyses on sediments from As hot spot areas in Taiwan and Vietnam suggest, comparable to previous studies, OM originates from both terrestrial and petroleum sources.
- Microcosm experiments on Taiwanese sediments indicate that the microbiological dissimilatory As(V) reduction is active in this aquifer, causing the release of As into the groundwater.
- As release in Taiwan sediment slurries is not controlled by an identified specific source of OM.
- Microbial community analyses of the Vietnam sediments do not reveal microbial communities associated with Fe(III) or As(V) reduction.

REFERENCES

- Al Lawati, W.M., Rizoulis, A., Eiche, E., Boothman, C., Polya, D.A., Lloyd, J.R., Berg, M., Vasquez-Aguilar, P and van Dongen, B.E. 2012. Characterisation of organic matter and microbial communities in contrasting Holocene and Pleistocene arsenic-rich aquifers, Red River Delta, Vietnam. *Appl. Geochem.* 27, 315–325.
- Berg, M., Trang, P.T.K., Stengel, C., Buschmann, J., Viet, P.H., Van Dan, N., Giger, W., Stüben, D., 2008. Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction. *Chem. Geol.* 249, 91–112.

- Gault, A.G., Islam, F.S., Polya, D.A., Charnock, J.M., Boothman, C., Chatterjee, D., Lloyd, J.R., 2005. Microcosm depth profiles of arsenic release in a shallow aquifer, West Bengal. *Mineral. Mag.* 69, 855–863.
- Héry, M., van Dongen, B.E., Gill, F., Mondal, D., Vaughan, D.J., Pancost, R.D., Polya, D.A., Lloyd, J.R., 2010. Arsenic release and attenuation in low organic carbon aquifer sediments from West Bengal. *Geobiology* 8, 155–168.
- Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D., Lloyd, J.R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* 430, 68–71.
- Polya, D.A., Mondal, D., Giri, A.K., 2010. Quantification of Deaths and DALYs Due to Chronic Exposure to Arsenic in Groundwaters Utilized for Drinking, Cooking and Irrigation of Food-Crops, in: Preedy, V.R., Watson, R.R. (Eds.), *Handbook of Disease Burdens and Quality of Life Measures*. Springer New York, pp. 701–728.
- Polya, D.A., Gault, A.G., Diebe, N., Feldman, P., Rosenboom, J.W., Gilligan, E., Fredericks, D., Milton, A.H., Sampson, M., Rowland, H.A.L., Lythgoe, P.R., Jones, J.C., Middleton, C., Cooke, D.A., 2005. Arsenic hazard in shallow Cambodian groundwaters. *Mineral. Mag.* 69, 807–823.
- Postma, D., Larsen, F., Hue, N.T.M., Duc, M.T., Viet, P.H., Nhan, P.Q., Jessen, S., 2007. Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling. *Geochim. Cosmochim. Acta* 71, 5054–5071.
- Ravenscroft, P., Brammer, H., Richards, K., 2009. *Arsenic Pollution*, first ed. Wiley-Blackwell, Oxford, UK.
- Rowland, H.A.L., Polya, D.A., Lloyd, J.R., Pancost, R.D., 2006. Characterisation of organic matter in a shallow, reducing, arsenic-rich aquifer, West Bengal. *Org. Geochem.* 37, 1101–1114.
- van Dongen, B.E., Rowland, H.A.L., Gault, A.G., Polya, D.A., Bryant, C., Pancost, R.D., 2008. Hopane, sterane and n-alkane distributions in shallow sediments hosting high arsenic groundwaters in Cambodia. *Appl. Geochem.* 23, 3047–3058.