MICROBIALLY MEDIATED ORGANIC MATTER DEGRADATION RELEASES ARSENIC INTO SE ASIAN GROUNDWATER

Richard D. PANCOST[1], Helen A. L. ROWLAND[2], Bart E. VAN DONGEN[1], Jon LLOYD[2] and Dave A. POLYA[2]

[1] Organic Geochemistry Unit, Bristol Biogeochemistry Research Centre, University of Bristol, School of Chemistry, Cantock's Close, Bristol, BS8 1TS, United Kingdom; [2] School of Earth Sciences, University of Manchester, Manchester M13 9PL, United Kingdom

Elevated arsenic in groundwaters exploited for irrigation and drinking water is significantly and detrimentally affecting human health in West Bengal, Bangladesh and other regions of SE Asia. A key mechanism for the genesis of arsenic in these waters is microbially mediated reductive dissolution of arsenic-bearing Fe(III) hydrated oxides (Islam et al., 2004). The role of organic carbon, whether from *in situ* organic matter (OM), i.e. OM from within the sediment, or from other sources, is widely recognised. Despite this, there is a paucity of data about the characteristics of OM in these arsenic-rich aquifers and little experimental evidence directly evaluating how OM oxidation is coupled to arsenic release. To investigate this, we characterised OM in several groundwater arsenic "hotspots" in West Bengal and Cambodia. We then conducted microcosm experiments in which OM degradation, iron reduction and co-occurring arsenic release and changes in the bacterial populations were analysed and compared.

In the first stage of this research, we extracted and analysed the lipid biomarkers in seven different sediment horizons (from 0 to 30 m depth) from a West Bengal arsenic "hotspot". This revealed that some of the OM present is characteristic of the original marginal marine depositional environment. However, in all but the most shallow sample, this was overprinted by abundant hydrocarbons with thermally mature (e.g. petroleum) distributions. These hydrocarbons included *n*-alkanes with no odd-over-even predominance and thermally mature distributions of hopanes and steranes. The presence of this previously unreported source of organic carbon is important as it has the potential to promote microbial activity and associated arsenic release. Indeed, in sandy horizons, the presence of large unresolved complex mixtures and relatively low abundances of *n*-alkanes suggest that indigenous microbes within the aquifer are degrading the petroleum and utilising it as a carbon source. The microbes present in these samples are diverse but include a significant population of *Sulfurospirillum* sp., a known As(V) reducer, providing the first evidence of such organisms mediating arsenic release from West Bengali aquifers.

To determine if this petroleum affects As (III) reduction, we conducted microcosm experiments under reducing conditions and using As-contaminated Cambodian sediments. Arsenic release and iron reduction did not occur in autoclaved sterile microcosms, clearly indicating that these reactions are microbially mediated. In unamended microcosms, arsenic release did occur in a sand-dominated sediment with a relatively low TOC content (0.1%) but containing petroleum-related hydrocarbons (SYII28). However, in a clay-dominated sediment with a relatively higher TOC content (ca 0.6%) but lacking petroleum-related hydrocarbons (SYII9), As release was not observed. Addition of acetate to this sediment caused As to be released at levels comparable to those in the unamended SYII28 sediment microcosm. This demonstrates that (1) the addition of labile OM does stimulate As release, but that (2) with respect to sedimentary OM, it is the type of OM present, not necessarily its total abundance, that governs the magnitude of arsenic release. However, this experiment did not test whether the OM (either petroleum in the unamended sediment or acetate when added as a supplement) is acting as a substrate for the growth of As-reducing microbes or whether it accelerates arsenic release by acting as an electron shuttle.

To determine if petroleum is degraded in these sediments under reducing conditions and co-occurs with As and Fe reduction, we conducted a further set of microcosm-based techniques, using the aforementioned suite of seven West Bengal sediments. As with the previous experiments, arsenic release and Fe(III) reduction was microbially mediated. Moreover, in all seven experiments petroleum *n*-alkane abundances decreased both in total concentration and relative to terrestrially sourced autochthonous organic matter. This strongly suggests that the microbial oxidation of petroleum-related *n*-alkanes could drive Fe(III) reduction and arsenic release.

The implications of this research could be profound. The mechanism by which extensive groundwaters in SE Asia have become contaminated by arsenic is hotly debated but critical to resolving what has been described as a human health catastrophe. Although many questions remain, this work suggests that natural petroleum seepage could be an important control on arsenic release and provide a guide for addressing this challenge.

REFERENCES

Islam, F.S. et al. *Nature* **430**, 68-71 (2004).