## 4.65.24

# Environmental impact assessment of forest and mining waste interactions in the Tamar River catchment

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The Tamar valley area in SW England is a highly mineralised region and the mines located in the valley were some of the largest producers of copper and arsenic globally in the 19$^{th}$ century. Now abandoned, the former mining sites are mainly used for economic timber production and farmland. However, the mining activity has left a legacy of As contamination (range 120-52600 ppm) waste in local soils and on unvegetated spoil heaps [1]. Trees across these sites can potentially act to stabalise mass movement of mining waste but vary in health. This project is to investigate mine waste and forest interactions in two coniferous sites of differing vegetation health within the Devon Great Consols Mine.

The relative contributions of different pollutant sources transported by streams that flow through the two catchments are being quantified in order to qualify the effectiveness of tree stabilisation. Monthly sampling regimes have been implemented to identify seasonal trends in sediment movement and water chemistry. Sediment finger-printing techniques [2] are currently being employed to identify and characterise potential contamination sources. This will allow the determination of source provenance of bedload and suspended sediment transported by streams.

Preliminary results show stream bed, suspended and bank derived sediments have high levels of As (> 9,000 ppm) and Cu (> 2,000 ppm). These levels are similar to concentrations in samples of mine waste spoil and mining-derived soil. Streamwater chemistry shows some variation between the healthy area (pH 6-7, Cu < 1 ppm, As < 0.1 ppm) and the unhealthy area (pH 4-5, Cu < 15 ppm, As < 0.25 ppm) but initial results indicate that the largest inventory of metals are being transported from the site in solid, rather than solute, form. The presence of As- and Cu- rich sulphides in the sediments entering the main streams and river will lead to an increase in solute fluxes over time and implies poor stabilisation in some areas.

### References

[1] Kavanagh P.J., Farago M.E. (1997) *Chemical Speciation and Bioavailability* **9,** 77-81.

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## 4.65.31

# Reduction of Fe(III) by *Geobacter sulfurreducens* and the capture of arsenic by biogenic Fe(II) minerals

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Bengal, and other areas of southern Asia, face a massive humanitarian crisis as the result of extensive and unwitting use of arsenic-rich groundwaters as drinking and irrigation waters. Previous studies in our laboratory have provided direct evidence for the release and reduction of As(V), sorbed onto hydrated ferric oxides, into these groundwaters by Fe(III)-reducing bacteria. Sequencing of 16S rDNA clone libraries amplified by PCR from microcosms exhibiting maximal rates of As mobilisation, showed a microbial community dominated by Fe(III)-reducing bacteria most closely related to *Geobacter* species. Thus we have made a detailed analysis of the potential of a model *Geobacter*, *G. sulfurreducens* to reduce and mobilise As, via two possible mechanisms; (i) direct dissimilatory reduction of As(V), or (ii) indirect reduction by biogenic Fe(II). This organism was chosen because the full genome sequence is available for analysis, and contains an arsenic resistance operon that could also be involved in the reduction of As(V) to As(III).

Initial experiments showed that *G. sulfurreducens* was unable to conserve energy for growth via the dissimilatory reduction of As(V). It was, however, able to grow in medium containing fumarate as the terminal electron acceptor in the presence of 0.5 mM As(V). However, we found no evidence of As(III) in culture supernatants using IC-ICP-MS, suggesting that arsenic resistance was not mediated by the arsenic operon, which relies on intracellular reduction of As(V) and the efflux of As(III). When the cells were grown using soluble Fe(III) as an electron acceptor, Fe(III) reduction resulted in the precipitation of the Fe(II)-bearing mineral vivianite after two weeks. This was accompanied by the removal of As from solution. XAS analysis of the vivianite indicated sorption of arsenic as As(V) (85%) and As(III) (15%). The occurrence of reduced As(III) was also confirmed by XPS, and was attributed to abiotic reduction of As(V) by biogenic Fe(II). When grown using insoluble ferrihydrite as an electron acceptor, Fe(III) reduction resulted in precipitation of magnetite, again accompanied by nearly quantitative removal of arsenic.

These results demonstrate that *G. sulfurreducens*, a model Fe(III)-reducing bacterium, does not reduce As(V), despite the genetic potential to mediate this transformation. However, the reduction of Fe(III) led to the formation of Fe(II)-bearing phases that are able to capture arsenic species.