Effect of groundwater flow on dissolved As in a Bangladesh aquifer

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The hydrological and geochemical factors that regulate the partitioning of sediment and groundwater As in an aquifer with mobilizable As are not well understood. Recent work conducted in Bangladesh suggests that groundwater residence time may be an important factor controlling the spatial distribution of arsenic [1, 2].

To better characterize these factors and their potential relationship, a three dimensional array of monitoring wells was installed in a sandy, raised village and in adjacent agricultural fields covered with silt and silty clay bordered by a small stream. Dissolved As concentrations increase dramatically from <5 to 500 μg L^{-1} over the 300 m distance separating the village and the stream. A strong redox gradient, with increasingly reducing conditions towards the stream, is indicated by groundwater Fe and SO_4 concentrations and sediment FeII/Fe ratios.

Head measurements over the area show that the annually averaged groundwater flow is from the village towards the stream. Between the peak of the dry season and the onset of the monsoon, the hydraulic gradient reverses and groundwater flows from the stream towards the village. $^3H/^3He$ ages and vertical hydraulic head gradients indicate areas of rapid vertical recharge in the village and fields, with older water (10 to 30 yr) occuring near the stream. The role of groundwater flow dynamics in establishing the redox and As gradient is currently under investigation.

Field and batch adsorption experiments suggest the sediment-groundwater partitioning (Kd) decreases toward the stream. The observed decrease in Kd may be linked to the increasing reducing state of sediment along the transect, the input of sulfate with recharge within the village, or a combination of both.

[1] Stute *et al.* (2007) *Water Resour. Res.* **43**, W09417. [2] van Geen *et al.* (2008) *Environ. Sci. Technol,* **42**(7) 2283-2288.

Benthic boron isotopes and glacial CO_2

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The cause of glacial-interglacial CO_2 variations remains an unsolved problem. While changes in deep ocean carbon storage are invoked in all current models, the causal mechanisms are unclear. Robust proxies for the ocean carbonate system are therefore required to allow us to track the magnitude and timing of changes in deep ocean carbon storage, and how these relate to the ice core CO_2 record.

Boron isotopes in benthic foraminifera should record deep ocean pH. We have developed a technique for measuring boron istopes by MC-ICPMS [1]. This methodology overcomes several problems encountered with earlier NTIMS measurements, and has been further refined to allow accurate measurements of the small numbers of benthic foraminifera typically found in deep glacial-aged sediments. As few as 5 benthic tests (~5 ng boron) may now be measured with an external reproducibility of < 0.3 ‰ (95% confidence), equivalent to < 0.03 pH units.

We have tested our understanding of the $\delta^{11}B$-pH proxy with a thorough core-top study of a range of benthic species, spanning ambient living conditions from pH 7.4 - 8.2, and 1 - 20 °C. All $\delta^{11}B$ values for epifaunal species show a close match to predicted $\delta^{11}B$ of $B(OH)_4^-$ in seawater [2], and infaunal species show offsets to lower values indicative of calcification from more acidic pore-waters. Despite differences in B/Ca ratios between species, we find no evidence for a vital effect on boron isotopes, nor for any incorporation of $B(OH)_3$, nor a significant temperature effect on the isotopic fractionation factor. We also see no change in $\delta^{11}B$ with sample size or apparent dissolution.

These results provide strong evidence that our understanding of the $\delta^{11}B$-pH proxy is sound. Further, our ability to measure small numbers of foraminifera, and combine different sizes, preservation states, and even different epifaunal species highlights the enormous potential of boron isotope measurements for palaeoceanographic studies of the carbon cycle. We will further demonstrate this with a number of LGM to Holocene time series from several key locations.

[1] Foster (2008) *EPSL* **271**, 254-266. [2] Klochko *et al.* (2006) *EPSL* **248**, 261-270.