Biogeochemical controls on dissolved trace elements in rivers

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Much of our understanding of controls on dissolved trace elements in rivers has come from global or broad regional surveys of a wide variety of rivers. These studies tend to emphasize the importance of factors such as lithology (e.g. Palmer and Edmond, 1993), weathering processes (e.g. Murnane and Stallard, 1990), or adsorption (e.g. Shiller and Boyle, 1985). However, recent work examining seasonal variability of trace elements within given river systems suggests that biologically-mediated redox processes also play an important role (Pontér *et al.*, 1992; Shiller, 1997). We have been examining fluvial dissolved trace element variability by field surveys, laboratory experiments, and modelling. Our results suggest that biologically-mediated reducing processes in source regions as well as in-stream biological oxidation processes are important in the seasonal regulation of certain trace elements.

Our field work involves the weekly or monthly sampling of a variety of rivers in the U.S. Our most detailed seasonal surveys (and the surveys having the most ancillary data) are for the lower Mississippi River and the Loch Vale Watershed (Rocky Mountain National Park), though other rivers in California, Mississippi, South Carolina, and Montana have also been sampled.

The Loch Vale Watershed is a small (~600 ha) seasonally snow covered catchment. Weekly samples have been collected at the outlet of a small alpine lake at 3050 m elevation. The dissolved trace element data show significant seasonal changes that appear to be linked to the seasonal snow cover and its effects on the redox chemistry of the lake and its sediments. Mn is high in the wintertime and low in the spring and summer. This is in accord with longer wintertime lake water residence times and probable associated reducing conditions. Mo shows an opposite cycle, compatible with its removal in reducing systems and remobilization during oxidizing conditions. U and Cu both show increases in the early spring when the beginning thaw flushes soil water from the watershed. Other data show DOC also increasing at this time of year (Baron *et al.*, 1991), suggesting that the flushed soil U and Cu may be complexed by humic substances or colloidal organics.

Data from other rivers of moderate size indicates that Mn and Mo frequently follow opposite seasonal trends. We also observed opposite behaviour of these two elements when following water downstream in the heavily dammed Tennessee River watershed. This behaviour is consistent with the opposite redox behaviours of these two elements (Mn becoming more soluble and Mo becoming less soluble when reduced) as affected by reducing environments within watersheds.

In the lower Mississippi River, dissolved Mn and Fe were found to increase rapidly in the fall and then decrease in the spring (Shiller, 1997). Zn and Pb follow a similar trend with lower relative changes in concentration. V and Mo follow an opposite seasonal trend (i.e. high in summer and low in winter). Hydrologic factors as well as changes in pH and suspended load cannot account for the seasonal variability of the dissolved trace elements. Variability in reducing environments (similar to that observed at Loch Vale) probably accounts for the seasonal changes in V and Mo. However, this seems an unlikely explanation for Mn and Fe which would likely be oxidized and removed to the particulate phase during transit from upstream sources to our sampling location in the lower river. That temperature varies inversely with dissolved Mn and Fe suggests that temperature-related changes in heterotrophic oxidizing activity could explain the seasonal variability of these two metals.

Our experimental work has focused on microbial Mn oxidation. Laboratory experiments using poisoned and unpoisoned river water demonstrate that microbial manganese oxidation is occurring in the Mississippi River. Furthermore, this oxidation process is strongly temperature-dependant, having an optimum around 30°C. Oxidation rates are high enough so that Mn appears to be rapidly cycled between the dissolved and particulate phases. These experiments suggest that environmental temperature changes affect the steady state balance between bacterial oxidation and reductive dissolution with concomitant effects on other trace elements. We have also found that the Mn oxidation process is occurring in the Pearl River (Mississippi) at similar rate to that observed in the lower Mississippi River. These two rivers are very different in their chemistry and hydrology, suggesting that microbial Mn oxidation in rivers is a common process.

Attempts to perform similar experiments with Fe have been less successful. For this element stabilization of Fe(II) by organic matter probably plays an important role in limiting the rate of oxidation of Fe by O_2 or H_2O_2. This stabilization would allow (temperature-dependant) heterotrophic activity to determine Fe cycling either by microbial Fe(II) oxidation or by oxidation of the stabilizing organics.

To better examine the importance of microbial Mn oxidation in controlling fluvial dissolved Mn concentrations, a simple numerical model was constructed. The model represents changes in dissolved Mn as a balance between input and removal processes. For the Mississippi River model, the input is held constant and the removal is a first-order process with the temperature-dependent removal rate constant derived from our laboratory experiments. The measured river water temperature is used to estimate the removal rate constant each day; thus, the only adjustable parameter is the constant input rate. The results of this model indicate that microbial Mn oxidation can explain the general timing and magnitude of the seasonal Mn cycle in the Mississippi River.

A similar model was also applied to the Pearl River. This river has a nearly opposite seasonality in dissolved Mn as compared with the Mississippi River. However, the discharge is also highly seasonal, indicating that dilution probably needs to be accounted for in our model. Therefore, the input was scaled to the discharge to give a constant input flux diluted by the changing river discharge. Temperature-dependant first-order Mn removal (based on our lab experiments) again was used to balance the input. This model explained well the seasonal variability of dissolved Mn in the Pearl River.

We conclude that seasonal variability in source region reducing environments probably accounts for the variability of dissolved concentrations of elements such as Mo and V that are made less soluble by reduction. For Mn and Fe, reducing environments (e.g. stratified lakes, bogs, etc.) are only important for concentration variability when those environments are near the sampling site; otherwise, seasonal variability is likely controlled by heterotrophic activity within the river that affects the oxidation process. Variability of strongly sorbed elements such as Pb and Zn appears to be tied to the variability of Mn and Fe.

References

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