

## Trace-metal mobility during $\text{KMnO}_4$ oxidation of TCE: Column experiments

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### Introduction

*In situ* chemical oxidation (ISCO) of chlorinated-solvent contamination in aquifers by  $\text{MnO}_4^-$  may cause significant changes in the redox, pH and mineralogical properties of the system. The potential influence of these changes on trace-metal mobility has been investigated using column experiments that simulate ISCO of TCE by  $\text{KMnO}_4$  under variable pH conditions.

### Experimental Methods

Unbuffered silica sand and calcite-buffered sand columns were constructed with nine sampling ports along their 50 cm length. Separate aqueous solutions of  $\text{KMnO}_4$  (307 mg/L containing Cu, Pb, Zn, Mo, Ni, and Cr at 1 mg/L) and TCE (43 mg/L) were supplied to the columns, and allowed to mix at the inlet. Aqueous samples were collected weekly and pH, Eh, alkalinity, major ions and trace metals were determined. Polypropylene threads were packed with the sand in the columns to provide an inert substrate to collect the insoluble Mn oxide reaction product for analysis by analytical TEM.

### Results and Discussion

The pH ranged from 2.40 in the unbuffered column to 6.25 in the buffered column. The aqueous geochemical data demonstrate that under all pH conditions, Mo, Pb, Cu and Ni are attenuated from the aqueous phase within the first few cm of the columns. In contrast, the concentration of Zn is not significantly attenuated and Cr concentrations remain constant implying conservative behavior. Discrete analyses of the Mn oxide phase by TEM/EDS indicate that the trace metals are directly associated with the Mn oxide.

### Conclusions

The experimental results indicate that within the pH range 2.40 to 6.25, the trace metals Mo, Pb, Cu and Ni are effectively sequestered by the Mn oxide reaction product while Zn and Cr are conserved in the aqueous phase.

## Atmospheric/soil $\text{CO}_2$ consumption at Coweeta Hydrologic Laboratory, western North Carolina, USA

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Atmospheric/soil  $\text{CO}_2$  consumption has been calculated using watershed flux-based mass balance methods for Coweeta Hydrologic Laboratory in western North Carolina. The study area watersheds are located in a humid temperate climate and are developed on granitic bedrock. The methods of this study differ significantly from previous studies of  $\text{CO}_2$  consumption because accurate watershed solute flux-based mass balance calculations permit  $\text{CO}_2$  consumption to be attributed exclusively to the silicate minerals that are weathering. The weathering of silicate minerals is a natural mechanism by which atmospheric  $\text{CO}_2$  is consumed on geologic timescales ( $>10^5$  years).

At Coweeta, no carbonate minerals are present in the bedrock, and chemical weathering is attributed to plagioclase feldspar, almandine garnet, biotite, and allanite. If it is assumed that carbonic acid is solely consumed by the weathering of these minerals, then  $\text{CO}_2$  consumption values range from 890 to 1300 moles/hectare/year for the three watersheds investigated. These  $\text{CO}_2$  consumption rates are lower than those reported in the literature for other localities, often by as much as an order of magnitude.

For Watershed 2 (W2) at Coweeta, bicarbonate data are available.  $\text{CO}_2$  consumption in W2 based on the stream bicarbonate flux is 640 moles/hectare/year, approximately a factor of two lower than the  $\text{CO}_2$  consumption calculated from the mineral weathering rates (1300 moles/hectare/year). This difference likely reflects that mineral weathering at Coweeta is consuming acids other than carbonic. Other acids may originate from atmospheric deposition, or from sulfuric acid produced by the weathering of pyrite.

Relatively low  $\text{CO}_2$  consumption by silicate weathering at Coweeta may reflect the temperate climate of the region, and/or being underlain by granitic bedrock. However, it is also possible that other methods which calculate  $\text{CO}_2$  consumption by separating carbonate-derived bicarbonate from silicate-derived carbonate may overestimate  $\text{CO}_2$  consumption.