



## Project Summary

# Early Diagenesis and Chemical Mass Transfer in Lake Erie Sediments

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Vertical profiles of pore water and sediment solids chemistry were obtained from two sites in Lake Erie. Samples were collected using both gravity coring and pore water "peeper" techniques. In general, concentrations of nutrients and toxic metals in sediment solids decreased with increasing depth. Comparisons of pore water "peeper" data to gravity core data showed that "peeper" data provides higher resolution near the sediment-water interface. Modifications of the present "peeper" are required to adequately sample easily oxidizable materials (e.g., ammonia, ferrous iron).

The thermodynamic tendency of metal phosphate and carbonate mineral phases to precipitate in Lake Erie sediments has been calculated by means of an ion-pair model of the interstitial water chemistry. The calculations suggest that detrital calcite, aragonite, and dolomite should be dissolving in the sediments, but that iron and manganese carbonates should be precipitating. Regenerated phosphate should be reacting with calcium, iron, manganese, and lead to form authigenic mineral phases. Whitlockite ( $\text{Ca}_3(\text{PO}_4)_2$ ) and not hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) is the predicted mineral phase controlling phosphate solubility. Zinc and cadmium are apparently controlled by other mechanisms, perhaps by sulfide phases, mixed mineral phases, adsorption and/or ion exchange equilibria.

Rates of anaerobic decomposition of Lake Erie sediments from one locality were determined for seven depth intervals at three temperatures. Sealed sediment sections were incubated under anoxic conditions and the interstitial waters were sampled over a period of approximately 200 days. Concentration increases of bicarbonate, phosphate, ammonium, calcium, magnesium, iron, and manganese in pore water within any given depth interval followed zeroth order kinetics and exhibited Arrhenius temperature dependency. The rates and energetics of these fermentation reactions are only slightly less than those reported from sediments undergoing sulfate reduction. The observed release rates decrease exponentially with depth in the sediment due to a corresponding decrease in the amount of oxidizable organic matter and acid hydrolyzable mineral phases.

*This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Lacustrine sediments are known to play an active role in the biogeochemical cycling of materials. Freshwater sediments act as both a source and a sink for many biologically important materials, notably nutrients, such as phosphorus,

carbon, nitrogen, sulfur, and silicon. Further, sediments are known to play an important role in resulting cycles of trace metals, radionuclides, and xenobiotics. Because of this, knowledge of the early chemical diagenesis of sediments, that is those reactions occurring during and after burial, is essential to an understanding of materials cycling in freshwater environments.

This study focused on the chemistry of nutrient and metal release during early diagenesis, rates of nutrient and metal regeneration, rates of materials' movement across the sediment-water interface, and the effects of bioturbation on materials' cycling.

The experimental approach was used; the nutrient and metal regeneration was studied in laboratory microcosms. Field observations of pore water chemistry and sediment solids chemistry were used to verify and test laboratory results.

Modeling indicates that 60% of the observed bicarbonate release is the direct result of organic decomposition, that 20% of the release is from the dissolution of calcium carbonate mineral phases, and that the remaining 20% is from the dissolution of magnesium, iron, and manganese carbonate mineral phases.

Kinetic modeling of the observed production rates accurately predicts the vertical profiles of calcium, magnesium, iron, and manganese, but cannot quantitatively account for all the concentration differences of the nutrient elements carbon, nitrogen, and phosphorus. In addition to decomposition, increased depositional flux also apparently accounts for significant changes in concentrations of the nutrient elements in the near surface sediments. Consideration of organic decomposition in the calculation of anthropogenic loading of nitrogen to Lake Erie sediments decreases the estimate of anthropogenic loading by about a factor of two. Estimates of anthropogenic loadings of labile materials (carbon, phosphorus, sulfur) to lake sediments cannot ignore organic decomposition.

The flux of nutrients and metals from Lake Erie sediments to anoxic overlying water was studied in laboratory microcosms. Three cases were investigated: 1) homogenized sediment without worms, 2) homogenized sediment preconditioned by tubificid worm activities, and 3) natural lake cores. Flux estimates were made using both direct (concentration changes in the overlying water) and

indirect (pore water concentration gradients) techniques.

Sediments preconditioned by the activities of tubificid oligochaetes exhibited a higher flux of ammonia, but a lower flux of iron, soluble reactive phosphorus, and soluble reactive silica. The presence of tubificids had no effect on bicarbonate flux. Comparison of direct and indirect flux estimates showed that both types varied widely. In general, indirect flux estimates were higher than direct flux estimates. Reduced fluxes of iron and phosphorus in the presence of tubificids probably are due to their continuous subduction of surficial oxidized material prior to anoxia. The reduction of silica flux in the presence of worms cannot be presently explained. Fluxes observed in the natural lake core experiment were similar to those observed in the homogenized sediment with tubificids. Mineral equilibrium calculations performed for the pore water data collected in these experiments showed that the laboratory microcosms provided a reasonable representation of chemical conditions in Lake Erie sediments.

A one-dimensional time dependent reaction-transport model which considers production, adsorption, and diffusion was found to adequately predict ammonia and bicarbonate profiles in laboratory microcosms containing homogenized Lake Erie sediment and no tubificids.

## Conclusions

Thermodynamic modeling of interstitial waters is a useful technique for suggesting possible mineralogical controls on trace metals. Application of such a model to Lake Erie pore waters reveals that iron and manganese carbonates, phosphates, and sulfides are all forming in the sediments as well as chlorophyromorphite, a lead phosphate. No mineralogical controls for zinc and cadmium were clearly identified. The inclusion of organic complexes or complexes yet to be discovered in the thermodynamic model will not significantly improve the results. Additional complexing only serves to lower the ion activity products and hence the saturation indices. Predicted supersaturation would be decreased, but not by more than about a factor of two. Undersaturation of zinc and cadmium phases would increase. Mixed and sulfide mineral phases are the most likely mineralogical controls on zinc and cadmium. It is also possible that the controlling reactions

could be adsorption or ion exchange equilibrium. Until more sophisticated techniques for examining sediment solids are employed and until existing thermodynamic data is critically compiled and adopted, no further progress can be made on this problem.

Knowledge of the rate of anaerobic decomposition of organic matter and subsequent release of nutrients and metals to pore waters is essential to an understanding of early diagenesis and chemical mass transfer in sediments. In Lake Erie, anaerobic decomposition proceeds via fermentation reactions, primarily methane fermentation. The rates and energetics of these fermentation reactions are only slightly less than those reported from sediments in which sulfate reduction is the primary diagenetic pathway.

Both direct and indirect estimates of the flux of ammonia, iron, soluble reactive phosphorus (SRP), soluble reactive silica (SRS), and bicarbonate from lake sediments to anoxic overlying water exhibit a high degree of variability. Further, indirect flux estimates for redox sensitive materials (i.e., ferrous iron and SRP) may grossly underestimate the actual flux. The initial flux of iron and phosphorus from sediments to anoxic overlying water is strongly dependent on conditions at the sediment-water interface prior to anoxia in the overlying water. Sediments preconditioned by the activities of tubificid oligochaetes exhibited a higher flux of ammonia but a lower flux of iron, SRP, and SRS. The presence of worms had no effect on bicarbonate flux. The higher flux of ammonia in the presence of worms appeared to be due to a worm-caused ammonia source in the upper zone of sediment. Reduced fluxes of iron and phosphorus in the presence of tubificids is most likely due to their continuous subduction of surficial oxidized material prior to anoxia. The reduction of SRS flux in the presence of worms cannot presently be explained.

Inclusion of diffusive loss of trace metals from sediments in mass balance calculations shows that Cu, Pb, and Zn are lost from sediments in roughly the same molar ratio as they accumulate in sediments. Even if the loading of Cu, Pb, and Zn to Lake Erie were to increase exponentially for the next 100 years, the concentration of these metals in the lake's waters would increase by only a factor of three to five.

Consideration of organic decomposition in the calculation of anthropogenic

loading of nitrogen to Lake Erie sediments decreases the estimate of anthropogenic loading by about a factor of two. Estimates of anthropogenic loadings of labile materials (carbon, phosphorus, sulfur) to lake sediments cannot ignore organic decomposition.

A one-dimensional time dependent reaction-transport model which considers only production, adsorption, and diffusion was found to adequately predict ammonia and bicarbonate profiles in laboratory microcosms containing homogenized Lake Erie sediment and no tubificids. More complex models are required for other parameters (iron, phosphorus, silicon) and situations (homogenized sediment with tubificids, real lake sediments).

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*The complete report, entitled "Early Diagenesis and Chemical Mass Transfer in Lake Erie Sediments," (Order No. PB 82-247 602; Cost: \$16.50; subject to change) will be available only from:*

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