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Field Investigations of Trace Metal Effects on Lake Erie Phytoplankton Productivity

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ABSTRACT. *Responses of phytoplankton to trace metal and phosphate enrichments were made in pelagic Lake Erie surface waters over the time period of 1999–2003. All experiments employed trace metal clean sampling protocols. Bioassays were incubated over a 0.75–4 d period. Response was evaluated by measures of biomass (chlorophyll-a; chl-a), photosynthesis (using the carbon-14 technique), and dilution assays used to measure chl-a specific growth and grazing rates. Metals assayed were Cd, Co, Zn (5–50 nM) and Fe over the range of (20–100 nM). Phosphorus was added singly (0.1–1 µM) or in addition with Zn or Fe. The principle finding from this study was that the frequency of observed trace metal limitation in pelagic Lake Erie phytoplankton was low. Picoplankton (0.2–2 µm) responded most frequently to the metal enrichment; metals were as frequently toxic as they were stimulatory. Nanoplankton (2–20 µm) were nearly insensitive to metal enrichment as were the microplankton (20–210 µm). An EDTA chelated mixture of Fe, Cu, Zn, Co, Mn, and Mo did stimulate picoplankton chl-a production over 3 days and the growth and grazing rate of this important size fraction. Toxicity of Zn at 50 nM was observed; the presence of phosphate reduced inhibition by Zn at this concentration. The results suggest that trace metals are not as important over the short term as the availability of phosphorus in controlling phytoplankton productivity; however, trace metal enrichment can periodically have a stimulatory effect, particularly on the picoplankton size class.*

KEY WORDS: *Cadmium, cobalt, bioassay, iron, nutrition, phosphorus, phytoplankton, zinc.*

INTRODUCTION

"Lakes, despite being polluted with metal ions 10–100 times as much as the oceans from riverine and atmospheric inputs, are often nearly as much depleted in these trace metals as are oceans. Therefore, the elimination mechanisms in lakes must be more efficient than those in oceans. Larger productivities and higher sedimentation rates for particles are primarily responsible for the more efficient scavenging in lakes through adsorption of met-

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als on phytoplankton, and to a lesser extent, by other particles."

(Stumm and Schnoor 1995)

There has been much focus on trace metal (viz. Fe) influences on biological productivity in the oceans (cf. Chisholm and Morel 1991), driven by the ultimate need to understand global carbon cycling, yet large lakes may at times bear similar issues controlling trace metal geochemistry and its impact on biota. Application of stringent sampling techniques in the Laurentian Great Lakes and the observations of low ambient bioactive trace metal concentrations has stimulated (re)investigation of trace metal impacts on biological productivity in the Great Lakes (Twiss *et al.* 2000, Sterner *et al.* 2004, this study).

Trace metal geochemistry in lakes is dominated by flux into the lake (via atmosphere or riverine inputs) and subsequently to the sediment, the primary sink. The dominant removal mechanism that controls flux of trace metal to the sediment is the reaction with particles. In large lakes, biotic particles composed primarily of plankton, are the main geochemical agents that are able to regulate the concentration of trace metal in the water column (Sigg 1994).

Several lines of evidence indicate that phytoplankton in Lake Erie can be limited by the availability of trace metal during summer months. There exist low concentrations of total dissolved (< 0.2–0.45 µm) Fe and Zn in surface waters during thermal stratification. Fe distributions are heterogeneous in Lake Erie surface waters (range 2–62 nM Nriagu *et al.* 1996; 2.6–23.8 nM, Mioni *et al.* 2003; 2.7–404 nM, Porta *et al.* 2005). Most iron in the water column is particulate, as anticipated from an element with high surface reactivity, and particulate bound metal is an important factor in regulating the bioavailability of this metal in Lake Erie (Porta *et al.* 2005, Mioni *et al.* 2003). High levels of Fe enrichment in the hypolimnion during thermal stratification is linked to anoxic conditions capable of reducing iron oxyhydroxides in the sediments that can diffuse into the overlying water, and wind induced sediment resuspension of fine-grained minerals (Nriagu *et al.* 1996). As such it is expected that a significant fraction of dissolved iron in Lake Erie will be complexed by strong Fe-binding organic ligands, as observed in oligotrophic ocean regions (Rue and Bruland 1995).

Like Fe, Zn shows heterogeneous distributions as evidenced by the measured values that range approximately an order of magnitude (0.31–3.8 nM; Nriagu *et al.* 1996). Zinc shows strong affinity to particles as shown by radio-tracer studies of ^{65}Zn scavenging by plankton from pelagic surface waters (Twiss and Campbell 1998a). The exceedingly low Zn concentrations relative to the loading (Nriagu *et al.* 1996) in Lake Erie suggests a high demand for this element by the plankton. Nriagu *et al.* (1996) hypothesize that the removal of Cd from the water column by plankton is in response to the high biological demand for Zn and the physiological substitution of Cd by phytoplankton (as observed for cultured marine phytoplankton subjected to low Zn concentrations; Price and Morel 1990).

There have been several earlier studies that have investigated trace metal impacts on Lake Erie phytoplankton from a nutritive perspective. Lange (1971) applied a bioassay approach wherein laboratory cultured species of phytoplankton (3 cyanobacteria, 1 chlorophyte) were added to lake water from the western basin that was amended with a combination of potential macro- and micronutrients. Inorganic phosphate (3.4 µM), Co (0.7 nM) and EDTA/citrate-chelated Fe were found to be growth limiting agents in 5 of 15 bioassays. In a series of experiments using lake water enriched with macronutrients (N, Si, P) vitamins, and an EDTA-chelated trace metal mixture, Hartig and Wallen (1984) showed that phosphate (0.81 µM) was limiting to the sampled phytoplankton community of the western basin in summer and that a chelated trace metal mix contained a limiting nutrient(s) in autumn. Storch and Dunham (1986) sampled water from the eastern basin and applied a bioassay and enriched lakewater approach to show that unchelated Fe enrichments of 0.2–0.9 µM occasionally enhanced photosynthesis yet were as often inhibitory. More recently (and using trace metal-clean sampling protocols), Twiss *et al.* (2000) used an enriched lake water approach to show that unchelated Fe (20–200 nM) could periodically enhance planktonic photosynthesis and biomass in the eastern basin and that chelated Fe additions and phosphate (0.2 µM) could support growth greater than controls and greater than phosphate enrichment alone.

Phosphorus availability is commonly considered the single limiting nutrient for phytoplankton productivity in Lake Erie, yet trace metal bioavailability may be a significant co-limiting or limiting nutrient during certain periods when its availability influences community composition. Our objective in this study was to determine the existence and extent of trace metal limitation among phytoplankton