Micronutrient Dynamics in Lakes and Their Investigation Using New Isotopic Tools.

Tom Johnson
University of Illinois at Urbana-Champaign
Micronutrients

- Iron - Fe
- Manganese - Mn
- Zinc - Zn
- Copper - Cu
- Boron - B
- Cobalt - Co
- Cadmium - Cd
- Nickel - Ni
- Molybdenum - Mo
- Vanadium - V
- Selenium - Se
Micronutrients - Measurement

- Trace-clean methods needed
- Extreme sensitivity to contamination by ordinary materials (Fe, Zn, etc.)
- Good measurements only in the last 15 years
- Relatively few studies of trace element concentrations/limitation
Micronutrients—Limiting in the Great Lakes?

From Sterner, 2008.

• Review Paper: “On the Phosphorus Limitation Paradigm for Lakes”

“A large amount of observational and experimental data seems to contradict the phosphorus limitation paradigm and instead indicates that most lakes are co-limited by N and P as well as, perhaps, by Fe and other resources...an alternative is that even if P is ultimately limiting over multi-annual time scales, over shorter but still meaningful time scales, co-limitation of multiple nutrients is expected, and indeed is very common.”
Micronutrients - Limiting in the Great Lakes?

From Twiss et al., 2005.
Lake Erie Study; Fe, Zn, Co Cd; enriched incubations

“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.”

Picoplankton key role?
Micronutrients - Limiting in the Great Lakes?

From McKay et al., 2004:

“Low availability of iron and other nutritive trace metals may also constrain productivity in the North American Great Lakes. Despite its importance, the biogeochemistry of iron in the water column of lacustrine systems remains poorly characterized.”
Fe, Zn (Twiss et al., 2005)

Lake Erie water, spiked with P, Zn, Fe
Ship deck incubation
Zn (Intwala et al., 2008)

Lab study; defined medium (not lake water)

Cd and Co as substitutes
Micronutrients- My Survey

- Complex interactions between nutrients
- Micronutrients likely limiting at certain places and times
- Many questions remain
- Trace element-clean methods are difficult but are in place
Stable Isotope Geochemistry: 1993
Stable Isotope Geochemistry: 2013
Elements with gray shrouds: Only one stable isotope
A Quick Stable Isotope Review

- Heavy vs. light isotopes: Slight Chemical differences
- Bonding changes/chemical reactions tend to fractionate isotopes
- Sulfate, nitrate, chromate, selenate reduction: Lighter isotopes react more readily
A Quick Stable Isotope Review

- Kinetic fractionation: Differing Rates
- Equilibrium fractionation: Differing $\Delta G$
  - Heavier isotopes favored in the more strongly bonded environment
- **Redox reactions cause greatest shifts**
- Coordination and/or **ligand changes**
$\delta^{66}\text{Zn} / \delta^{64}\text{Zn}$ in marine particulate (lighter isotopes enriched in phytoplankton)

**Figure 4.** The $\delta^{66}\text{Zn}$ in marine particles trapped at 250, 1000, and 2500 m depth at the mesotrophic site of EUMELI (central Atlantic Ocean) from February 1991 to January 1992. The normal sampling interval is 10 days. Particle fluxes of 250 m depth. Repeated observations in spring and 2000 m and below. The graph represents the variation in $\delta^{66}\text{Zn}$ with depth and time.
$^{66}\text{Zn}/^{64}\text{Zn}$ and $^{65}\text{Cu}/^{63}\text{Cu}$ in seawater (Bermin et al., 2006)

Fig. 13. Concentration (□) and isotopic composition (■) vs. depth for Cu and Zn from station P4 (Lohan et al., 2002) in the North East Pacific Ocean.
$^{66}\text{Zn}/^{64}\text{Zn}$ in particulate, Lk. Greifen (Peel et al., 2009)

Fig. 3. Rayleigh (solid lines) and equilibrium fractionation (dotted lines) models (see Hoefs [2004] for relevant equations) for the uptake of dissolved Zn by algae in the epilimnion. The initial $\delta^{66}\text{Zn}$ value is $+0.1\%$, and the isotopic fractionation factor between algae and solution is $0.8\%$ (see text for detailed explanations). Also plotted are the measured $\delta^{66}\text{Zn}$ values in the settling particles at 28-m depth vs. the Zn remaining in the epilimnion using the data given in Fig. 2 and normalizing against the highest [Zn] measured on 25 January 1990 (2.20 $\mu$g L$^{-1}$).
$^{56}\text{Fe}/^{54}\text{Fe}$ in seawater - Bermuda

(John and Adkins, 2012)
Fig. 3. $\delta^{56}\text{Fe}$ (A) and Fe concentration (B and C) in dissolved and particulate fractions of seawater from stations 14 and 28, versus potential density. In A, the vertical grey bar indicates the crustal value ($0.07 \pm 0.02\%$, 2SD; Poitrasson, 2006). In B and C, the error bar is smaller than the symbols. Depths are indicated in B next to the data points. The large grey areas locate roughly the density of the water masses (SPEW, 13CW, AAIW; see text for details) and the Equatorial Undercurrent (EUC).
$^{29}\text{Si}/^{28}\text{Si}$ in Lk. Tanganyika (Alleman et al., 2005)

**FIG. 2.** Dissolved Si concentration (dashed line) and $\delta^{29}\text{Si}$ (bold line) profiles at station TK1 (northern basin), TK5 and TK8 (southern basin) collected in July 2002.
Micronutrients - Challenges for isotopic measurements

- Very low concentrations
- Large sample volumes - 10L?
- Prolonged prep, large volumes of reagents
- Contamination-prone
- Rigorous trace-clean procedures needed
- Mass Spectrometry is still an “art”
- Interferences, bias
Status Report: Isotopic indicators of micronutrient processes

- Challenging: Methods being developed
- A few marine data sets exist: Zn, Cu, Fe, Si
- Lake Data sets: Zn, Si
- Possible applications of natural variations:
  - *Uptake and regeneration processes*
  - *Identifying sources*
- Stable isotope tracers (spikes)?