The chemical speciation of Pb in the water column of Paul Lake (MI)

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We present and discuss the chemical speciation of dissolved Pb (Pb_d) in the water column of a small kettle lake located in the Michigan upper peninsula; Paul Lake. This lake offers a semi-permanent oxic/anoxic transition in the water column because its morphology, small surface area, and sheltering from dominant winds are conducive to the establishment of a biogenic meromixis. A more complete description of the lake can be found in Lienemann *et al.* (1997) where we have shown that, at the oxic/anoxic transition, Co is scavenged by the formation of MnO_x at the surface of manganese oxidizing bacteria. Here, we detail the speciation of Pb_d using a multi-method approach to characterize the various chemical forms under which lead is present.

Methods

Water samples were collected from a small boat by peristaltic pumping using a portable Masterflex pump equipped with acid-cleaned Tygon tubing. Samples were withdrawn into acid-cleaned polypropylene syringes without contact with the atmosphere using a three way valve, and stored in either cleaned 60 mL Nalgene bottles or acid-cleaned 16 mL polypropylene Falcom tubes, after filtration through acid cleaned Acrodis LC-PVDF Gelman filters. A fraction of the aliquots were preserved acidified for total dissolved analyses, and two other fractions were transported to the field laboratory for voltammetric and chromatographic separation/analyses.

Major and minor ions were analysed by titration, colorimetry, ICP, and capillary electrophoresis. Total $^{T}Pb_d$ was determined either by ICP-MS (VG-Plasmaquad 2+ or by Z-GAAFS (Varian SpectrAA-800 Zeeman). Metal titration curves were performed by DPASV using a Metrohm VA-663 stand in combination with an AIS LCP200, the separation of Pb associated with dissolved organic matter was accomplished using a tentacular DMAE resin packed in a peek column (EM Science).

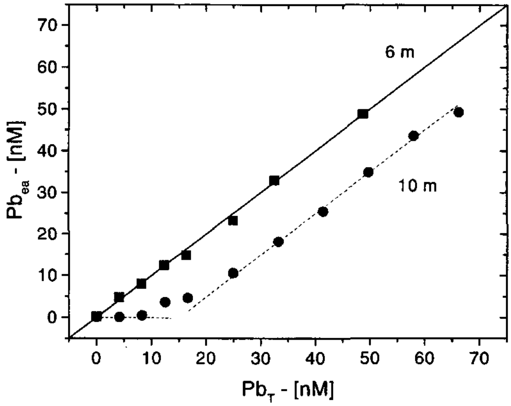

FIG. 1. Pb titration curve of anoxic and anoxic water samples in the water columnof Paul Lake (MI). The 1:1 line shows no significant complexation as it is the case in the oxic waters (6m), whereas below the oxic/anoxic transition (10m) Pb is complexed.

Results

The water column profiles of $^{T}Pb_d$, demonstrate a sharp concentration gradient below the oxycline. Through the oxic/anoxic transition $^{T}Pb_d$ concentrations increase from 200 pM to 1.8–3.7 nM at depth. Particulate Pb remained always small except in July 1995 where it peaked at 2nM just below the oxycline. Thermodynamic calculations report that PbS is oversaturated by about 4 orders of magnitude [SI = $\log(IAP/K_{sp})$ = 3.9], suggesting that a significant fraction of Pb_d must be complexed in the bottom anoxic waters. In addition, the concentrations of $^{T}Pb_d$ vary concomitantly with those of $^{T}Fe_d$.

Pb titration curves differ significantly across the oxic/anoxic transition. In oxic waters, our results indicate, within our analytical window, the absence of Pb ligands, whereas in the anoxic bottom waters, there is a significant Pb complexation. The interpretation of these titration curves, using either a nonlinear fitting procedure or the linearization method popularized by Ruzic (1982), suggests that a 1:1 complex forms between Pb and an unknown ligand (Fig. 1).

These results are confirmed by our chromatographic separation of Pb-DOM using the DMAE resin. They also are compatible with the new findings reported by Achterberg *et al.* (1997) on the complexation of metals in the anoxic bottom waters of the Esthwaite Water.

References

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