

# Pb adsorption and surface area of bacterially oxidized Mn

Y. M. Nelson

L. W. Lion

W. C. Ghiorse

M. L. Shuler

School of Civil and Environmental Engineering, Cornell University, Ithaca, New York, 14853, USA

Section of Microbiology, Cornell University, Ithaca, New York, 14853, USA

School of Chemical Engineering, Cornell University, Ithaca, New York, 14853, USA

Trace metal cycling in aquatic environments is controlled largely by adsorption to suspended particulate material (SPM) (1), and this process is governed predominantly by Fe and Mn oxides contained in the SPM (2). Initial estimates of the relative contributions of Fe and Mn oxides to Pb adsorption indicated that the role of Fe oxides far overshadowed that of Mn oxides based on measurement of the Fe and Mn content of natural surface coatings and adsorption of Pb by abiotically produced, laboratory surrogate Fe and Mn oxides (3). However, Mn oxides in circumneutral aquatic environments are likely to be of biogenic origin (4), and biologically oxidized Mn may exhibit a greater specific surface area and thus greater trace metal adsorption than abiotic Mn oxides. To test this hypothesis, in this work Mn was oxidized by the bacterium *Leptothrix discophora* SS-1 and the surface area and Pb adsorption of the resulting Mn oxides were determined and compared to those properties of abiotic Mn oxides.

## Methods

*L. discophora* SS-1 was grown in pure culture in 1-L shake flasks at 150 rpm in a defined mineral salts medium with pyruvate at 240 mg/L as the carbon and energy source. Vitamin B12 was added at 2  $\mu\text{g/L}$  as required for growth, and 0.1  $\mu\text{M}$   $\text{FeSO}_4$  was added as required for oxidation of 50  $\mu\text{M}$   $\text{Mn}^{2+}$  (5).  $\text{Mn}^{2+}$  was added as  $\text{MnSO}_4$  at a concentration of 50  $\mu\text{M}$ . Dissolved  $\text{Mn}^{2+}$  was determined by centrifuging the broth at  $13,400 \times g$  for 30 min. and measuring supernatant Mn concentration by atomic absorption spectroscopy (AAS) using a Perkin-Elmer Analyst 100 (Norwalk, CT, USA).

Two commercially available Mn oxides were examined for comparison to the biogenic Mn oxide, a chemically-derived  $\beta$ -phase Mn oxide (Fisher Scientific, Pittsburgh, PA, USA), and a powdered Mn dioxide (ICN Pharmaceuticals, K&K Laboratories, Plainview, NY, USA). Fresh, abiotic Mn oxide precipitates were also prepared by reacting

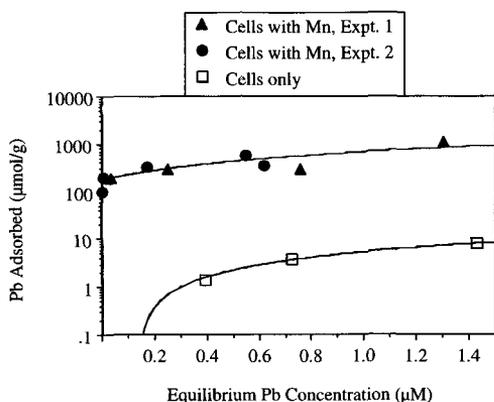


FIG. 1. Comparison of Pb Adsorption by *Leptothrix discophora* SS-1 with and without Mn oxide (log scale).

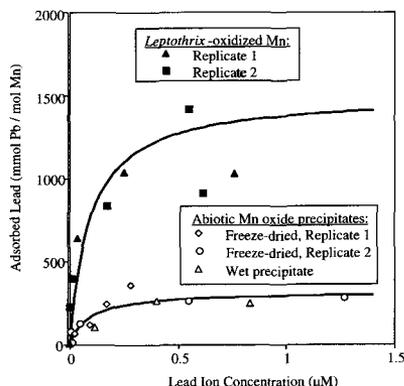


FIG. 2. Pb adsorption to Mn oxidized by *Leptothrix discophora* compared to Pb adsorption to fresh abiotically precipitated Mn oxides.

TABLE 1. BET surface area of biogenic and abiotic Mn oxides

Source of Mn oxide	BET Surface Area ( $\text{m}^2/\text{g}$ Mn oxide)	
	Average	Std. Dev. (n=3)
<i>Leptothrix</i> oxidized Mn	33.7	0.9
Fresh, abiotic Mn oxide precipitate	15.1	0.4
Crystalline powdered $\text{MnO}_2$ (ICN)	3.7	0.15
Crystalline $\beta$ phase $\text{MnO}_2$ (Fisher)	0.034	0.012

$\text{MnCl}_2$  with  $\text{KMnO}_4$  at  $90^\circ\text{C}$  under basic conditions.

Specific surface areas were measured with  $\text{N}_2$  gas adsorption from a mixture of 30%  $\text{N}_2$  and 70% He using a Quantasorb Sorption System (Syosset, NY, USA), and calculated using a single point B.E.T. method. Pb adsorption was measured by equilibrating Pb solutions with Pb concentrations ranging from 0.1 to  $4.0 \mu\text{M}$  (ionic strength = 0.05 M) with suspensions of Mn oxides in silanated glass beakers at  $25^\circ\text{C}$  and pH 6.0. After equilibrating for 24 h, suspensions were centrifuged at  $13,400 \times g$  for 30 min. and Pb concentrations in the supernatants were determined by graphite furnace AAS (GFAAS) using a Perkin Elmer (Norwalk, CT, USA) AAnalyst 100 equipped with a HGA 800 graphite furnace and an AS-72 autosampler.

## Results and discussion

The specific surface area of the biologically oxidized Mn was two times greater than that of the fresh abiotic Mn oxide precipitate and 1 to 3 orders of magnitude greater than that of the more crystalline Mn oxide

minerals (Table 1). These results suggest that the biologically oxidized Mn is highly amorphous.

Pb adsorption by *L. discophora* with Mn oxide deposits ( $0.3 \text{ mmol Mn/g}$  dry wt.) was two orders of magnitude greater than adsorption to *L. discophora* cells alone (Fig. 1, note log scale). This is consistent with previous reports that metal oxides bind Pb to a greater extent than organic materials (2).

Pb adsorption to Mn oxidized by *L. discophora* was about five times greater than Pb adsorption to a fresh abiotic Mn oxide precipitate (Fig. 2). The *Leptothrix*-oxidized Mn adsorbed several orders of magnitude more Pb than commercially obtained Mn(IV) oxides (Fig. 3). These results are consistent with the B.E.T. specific surface area measurements, with very low Pb adsorption observed for the more crystalline Mn oxide minerals (Table 1). Pb adsorption of the biologically oxidized Mn was also two orders of magnitude greater than that previously determined for colloidal Fe oxide deposits (Fig. 3) (6).

The results of this work indicate that Mn oxides may play a much greater role in controlling trace metal adsorption to SPM than previously thought and suggest a strong biological control on trace metals via biologically mediated redox reactions of Mn. Further, the high adsorption capacity of biologically oxidized Mn may lead to applications in removal of trace metals from contaminated waste streams.

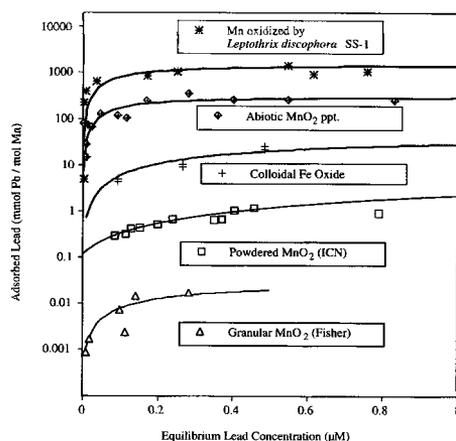


FIG. 3. Pb adsorption to *Leptothrix*-oxidized Mn compared to abiotic Mn oxide minerals and colloidal Fe oxide.

## References

- Kruaskopf, K.B. (1956) *Geochim. Cosmochim. Acta*, **9**, 1-24.
- Jenne, E.A. (1968) In: *Trace Inorganics in Water* R.F. Gould, Ed. (American Chemical Society, Washington, D.C., USA, **73**, 337-87.
- Y.M. Nelson, L. W. Lion, M. L. Shuler, W. C. Ghiorse, Presented at the Aquatic Sciences Meeting, Amer. Soc. Limnol. Oceanogr. Santa Fe, NM, USA (1997).
- W. Stumm, J. J. Morgan, *Aquatic Chemistry*, John Wiley and Sons, New York, NY, USA pp 465-468 (1981).
- Y. M. Nelson, L. W. Lion, W. C. Ghiorse, M. L. Shuler, *Appl. Environ. Microbiol.* **In Press** (1998).