

Zinc and Cadmium Associations with Reduced Forms of Sulfur in Organic Matter-Rich Aerobic Soils

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Unusually high natural concentrations of zinc and cadmium have often been associated with soils high in organic matter and sulfur. For example, the soils from the Manning region of Western New York and from Guelph in Ontario concentrate zinc and cadmium by biogeochemical processes using sulfur. Scientists at The Pennsylvania State University in University Park, Cornell University in Ithaca, New York, and the University of Wisconsin in Madison have determined the oxidation states of sulfur in bulk soils, the distribution of these two metals in soil particles, and their solubility, toxicity, and bioavailability. The researchers used spectroscopic, chemical, and bioassay approaches and illustrated how the macroscopic behavior of metals in soils can be explained by knowledge of their forms at the microscopic scale.



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Peat deposits, such as those overlying the dolomite bedrock that extends from eastern New York State into Ontario in Canada (**Figure 1**), contain unusually high concentrations of metals, such as zinc and cadmium, leading to potentially hazardous concentrations of cadmium in some crops. Scientists have determined that soluble zinc entered these wetlands by drainage and groundwater emanating from weathering dolomite [CaMg (CO₃)₂].

One possible concern with these metalliferous peats is the release of sulfur-bound cadmium and zinc during natural weathering conditions or when the bogs are drained for agricultural use. For example, in the Manning peatlands of western New York, this situation appears to have arisen as toxic metals were detected in vegetable crops in the early 1940s, not long after the bogs were drained for agriculture. Very high concentrations of zinc were measured in the plant shoots of some fields.

We recently collected peat soils from the Manning region and from Guelph in Ontario to investigate the processes controlling zinc and cadmium solubility, toxicity, and bioavailability in these soils.

Reduced forms of sulfur (compared to their oxidized forms) are potentially important to retain zinc and cadmium in organic soils. By using x-ray absorption near-edge spectroscopy (XANES) at NSLS beamline X19A, we have shown that 35 to 45 percent of sulfur in these soils exists in the most reduced electronic oxidation states 60 years after the soils were drained, while less than five percent of sulfur exist in the most oxidized forms (**Figure 2**). Although reduced forms of sulfur are not expected to prevail in aerobic soils for long periods of time, their presence may be the result of anaerobic microenvironments in otherwise apparent oxygen-rich soils, or of slow oxygen diffusion into soil aggregates.

Another technique called energy-dispersive x-ray absorption (EDX) also showed a close spatial distribution between zinc and sulfur in soil particles, thus suggesting their chemical association (**Figure 3**). But, despite this EDX evidence, conventional x-ray diffraction (XRD) analy-

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ses of the bulk soils did not detect a mineral phase of sphalerite (ZnS) in any of them.

Chemical data showed that cadmium binds relatively more strongly in these sulfur-rich organic soils than in most mineral soils, suggesting that reduced sulfur could be limiting cadmium solubility more than zinc. These data also showed that most of the high-zinc soils were very toxic to plants, and that such toxicity has persisted for decades since the soils were drained.

We have also demonstrated high zinc solubility and plant availability but relatively low cadmium solubility and plant uptake, despite very high soil cadmium concentrations, as well as both low mobility and bioavailability of cadmium relative to zinc in these soils.

We conclude that sulfur biogeochemical cycling may play an important role in zinc and cadmium retention in sulfur-rich organic soils.

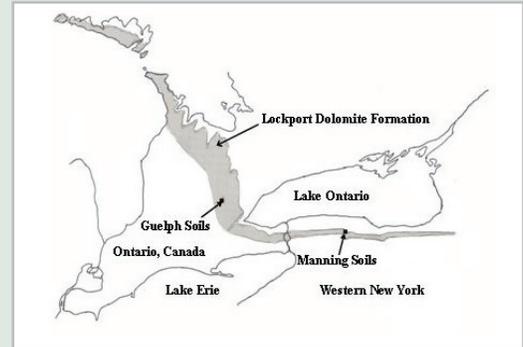


Figure 1. Lockport Dolomite formation: extension across New York and Ontario in Canada (gray area). The map shows the area where the Manning and Guelph peat soils were collected.

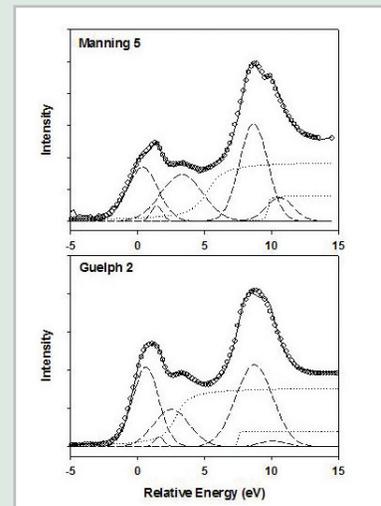


Figure 2. X-ray absorption near-edge spectroscopy (XANES) spectra for the Manning and Guelph soils used in this study. The solid line is the experimental spectrum, the circles represent the fit to the experimental spectrum, the broken lines are the Gaussian curves, and the dotted lines are the arctangents.

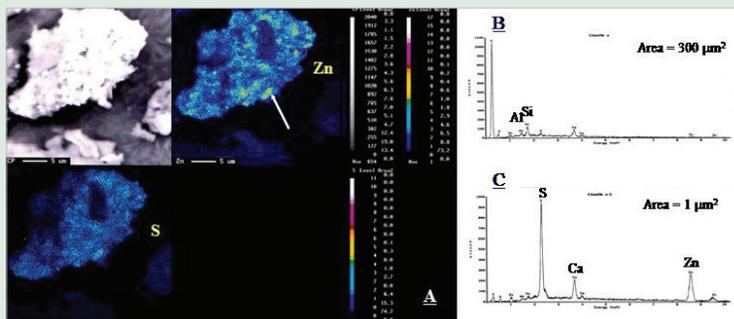


Figure 3. (A) X-ray maps obtained by energy-dispersive x-ray analysis (EDX), showing the backscattered image and the distribution of zinc and sulfur in a soil aggregate of the Manning soil containing 15800 milligrams of zinc per kilogram (top) and 7230 milligrams of sulfur per kilogram (bottom). (B) X-ray energy spectra showing the elemental composition of the whole aggregate (300-square-micrometer). (C) X-ray energy spectra showing the elemental composition of a one square-micrometer area (arrow in panel A) of the same soil particle.