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Salt effects on proton and cadmium binding to natural organic matter

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Sudden changes in the deposition of salts to soils may have dramatic effects on the chemistry of the soils and draining waters. Two examples are atmospheric sea-salt episodes in coastal areas and the spread of road salt to prevent ice formation during winter in temperate regions. The salt dependence of proton dissociation and metal binding to natural organic matter may be important in this respect.

For 5 organic soils, we conducted batch experiments at various ionic strengths to investigate whether proton dissociation and cadmium binding could be described with the mechanistic Stockholm Humic Model (SHM). The observed salt dependence of proton dissociation was stronger than predicted both by the original SHM [1] and by other currently used equilibrium models such as WHAM-6 [2] and NICA-Donnan [3], which rely on "generic" proton-binding parameters and electrostatic descriptions valid for isolated organic matter in solution. For the SHM, the fits for proton dissociation were improved considerably when the surface geometry of the solid-phase humic substances was changed from spherical to planar. Also Cd binding was reasonably well described with the revised SHM. However, for two poorly humified Sphagnum peats, the SHM could simulate Cd binding only if the heterogeneity parameter for cation complexation ΔLK_2 was decreased.

In conclusion, the salt dependence of proton dissociation and cadmium binding to solid-phase organic matter is stronger than that observed for dissolved organic matter. This has implications for the understanding of soil chemical effects as a result of inputs of road salt and sea salt.

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Sediment Fe mineralogy of 100 boreal forest lakes

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We have used ^{57}Fe Mössbauer spectroscopy to characterize the surface (0-2 cm) and pre-industrial (20-22 cm) sediments from the deepest parts of 100 lakes in the Rouyn-Noranda region of the Canadian boreal forest. Several depth profiles were also obtained. The samples were collected as part of the Geological Survey of Canada Metals in the Environment (MITE, Phase-I) program. This is the first such broad Mössbauer study, covering lakes with diverse characteristics (pH 4-9, sediment organic matter contents 5-80%) and from diverse settings (dominant vegetation type, catchment area rock type, various distances from a metal smelter point source, etc.). Several complimentary measurement techniques were used, along with standard geochemical and limnological measurements. The Mössbauer method was the most suited for resolving and quantifying the detrital and authigenic Fe phases, using spectral treatment and analysis methods developed at Ottawa.

The spectra collected at room temperature allow us to resolve and quantify (to ~1% of total Fe) the following populations: (1) total ferric and ferrous amounts, (2) common octahedrally coordinated ferrous silicates, (3) octahedrally coordinated ferric iron silicate contributions combined with the superparamegnetic (i.e., nanoparticulate) Fe oxyhydroxides, (4) magnetically blocked microcrystalline Fe oxides such as hematite and magnetite/maghemite mixtures, (5) certain specific mineral species, such as pyrite, epidote, ilmenite (not observed), and vivianite-like phosphates (not observed), that have distinct signatures, and (6) zero-valent metallic Fe, when present (see below). Spectra collected at cryogenic temperatures then allow further resolution of all known Fe oxide and oxyhydroxide phases.

First results from a subset of the lakes (and from a variety of marine sediments) established that the predominant reactive authigenic Fe oxyhydroxide phase was nanogoethite (nGt) rather than the expected ferrihidrite (Fh) or Fh-like phases [1]. The present study confirms this, with only a few cases of Fh dominance. A surprising occurrence of authigenic metallic α-Fe is documented in some deep samples that uniquely do not contain any detectable Fe oxyhydroxides. Also, in general, the authigenic phases and ferric/ferrous abundancies are not distributed according to monotonic diagenetic redox depth profiles.

References
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