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The retention of calcium, barium, and strontium ions by a mollisol humic acid: Spectroscopic investigation

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Humic substances have a major role in controlling the mobility and bioavailability of metallic ions in soils and natural waters. The alkaline earth metals, calcium, barium, and strontium, are broadly abundant in the crust of the earth, and Ca2+ ions are known to be important in the formation of structural aggregates in soils. Yet, direct spectroscopic evidence of how Ca, Ba, and Sr ions interact with soil organic matter, is minimal. To develop a deeper understanding of the interaction of the alkaline earth cations in soil, we studied the complexation behavior of strontium, barium and calcium by humic acid (HA) using solid-state 13C CP-MAS NMR, FTIR and extended x-ray absorption fine structure (EXAFS) spectroscopy. A HA sample was extracted from an agricultural mollisol (pH 6, 32.5% clay content, 3.7% organic carbon) located in southwestern Minnesota, USA, by the standard NaOH method. The HA sample was treated with chloride salts of Ca, Sr or Ba, then freeze-dried prior to spectroscopic measurements. The FTIR spectra, obtained using pressed KBr disks, and the 13C NMR spectra revealed spectral differences, stemming mainly from deprotonation reactions of the carboxylic and phenolic groups of the HA. The association of Ca, Ba, and Sr ions with the HA caused a marked FTIR shift of the carboxylate band, with the Ba shift being the most pronounced (HA 1604.7; HA-Ca 1595.1; HA-Sr 1597; HA-Ba 1579.6), which seems to imply that Ba is the strongest bound element. An NMR shift of the carbonyl peak at 171.8 ppm was also observed to 174.5 for Ca, 173.7 for Sr, and 174.4 for Ba confirming that these cations are behaving differently towards soil HA. The EXAFS spectra indicated back-scattering from oxygen atoms, in the first shell, for Ca, Sr, and Ba with varied coordination number. Our data prove that (1) the carboxylates and phenolates are the prevailing functional groups involved in the interactions between the extracted HA and alkali metal cations, (2) barium forms the strongest complex compared to strontium and calcium.