

The fate of phosphorus in biosolids treated soils: Speciation, transport and accumulation

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Fertilization of agricultural lands with biosolids contributes to phosphorus (P) inputs to surface waters. This occurs due to the common practice of addition to meet the N needs in crop production resulting in accumulation of high concentrations of soil P. The solubility, bioavailability and transport potential of P in soil varies according to the type of biosolid applied. We hypothesize that: (A) P loss to surface and ground water is determined by P speciation in biosolid treated soil; and (B) P speciation is a function of land management. Thus our specific research objectives in the proposed research are to evaluate P speciation as a function of: (a) soil depth, (b) crop cover (corn versus grass), and (c) fertilizer source: biosolid versus conventional P fertilizer. As the form of P present in biosolids is complex, a molecular-level assessment of P speciation in biosolid-treated soil will build our understanding of P reservoirs and their susceptibility for exchange with water. For the current study soils were collected from a field site in Rosemount, MN with a 20 year history of biosolid amendments followed by 25 years of crop production without biosolids. Soils were air dried, passed through 2 mm sieve and extracted for soil-P forms via sequential extraction technique. Soil samples were further used for P-X-ray absorption near edge structure (XANES) (bulk and nanometer-focused) spectroscopy measurement. Results from the extraction procedure predicted the enrichment of upper 0-30 cm soil layer with labile P fractions and suggest that Ca-P is predominant in the biosolid treated soil. This was also evident from the XRF maps which showed co-location of P with Si, Al and Ca. Principal component analysis of experimental P XANES spectra of $<3\mu\text{M}$ particle suggest that two P species are present: components X, Y, and Z were supported by target transformation analysis using reference spectra (Bohemite, Variscite and P adsorbed to ferrihydrite). Data of P (from spectroscopic measurements and wet chemistry) will allow us to better understand the P species in biosolid treated soils such that high agricultural productivity can be maximized and P loss to surface and ground waters minimized.

Hematite nanoparticle structure and reactivity

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Iron (hydr)oxide nanoparticles are widespread in the environment, and their high surface areas make them even more important to biogeochemical processes than expected from abundance alone. Recent research suggests that the reactivities of Fe (hydr)oxide nanoparticles with respect to sorption, dissolution, and redox reactions tend to be sensitive to particle size. In order to better understand the mechanisms controlling nanoparticle reactivity, we are characterizing bulk and surface structure and composition of hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles ranging in average size from 3.6 to 72 nm. This research uses a combination of techniques including: high resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD), thermogravimetric analysis (TGA), BET surface area analysis, X-ray photoelectron spectroscopy, magnetic characterization by superconducting quantum interference device measurements, extended x-ray absorption fine structure (EXAFS) spectroscopy, and high energy x-ray scattering (HEXS) with pair distribution function analysis.

XRD and HRTEM indicate that all of the samples are hematite with well defined crystalline structure. EXAFS, TGA and HEXS show progressive hydroxylation with decreasing particle size, and XPS confirms that the surfaces of smaller particles are more hydroxylated. This change in surface and near-surface structure and composition is likely an important factor behind differences in reactivity as observed by our group and others. Size resolved changes in magnetic properties could have important consequences for processes ranging from paleomagnetism to particle aggregation to interactions with microorganisms.