

**MECHANISMS OF PHOSPHORUS STABILIZATION IN THE SOIL
ENVIRONMENT: A MOLECULAR SCALE EVALUATION**

by
Stefan Hunger

A dissertation submitted to the faculty of the University of Delaware in partial fulfillment
of the requirements for the degree of Doctor of Philosophy in Plant and Soil Sciences

Fall 2003

© 2003 Stefan Hunger
All Rights Reserved

ABSTRACT

The mobility and bioavailability of phosphorus, an element widely considered to be the limiting nutrient for eutrophication in fresh water, is determined by its speciation in the natural environment. The speciation of phosphate in model systems of increasing complexity and in poultry litter was investigated using solid-state ^{31}P Nuclear Magnetic Resonance (NMR) and P K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy as molecular tools. The sorption kinetics and isotherms of phosphate were also investigated in these model systems.

The spectroscopic results indicate that phosphate sorbs to the gibbsite surface as a combination of binuclear, bidentate surface complexes and amorphous aluminum phosphate surface precipitates in the presence and absence of the competing organic acid citric acid and of the cooperatively adsorbing calcium cation. No aluminum phosphate surface precipitates are however observed in the model system containing both gibbsite and calcite as sorbents, but rather ternary surface complexes at the gibbsite surface at low surface concentrations, and a mixture of surface complexes at the gibbsite surface and a calcium phosphate precipitate at the calcite surface at elevated concentrations.

The results of the ^{31}P -NMR-spectroscopic investigation of unamended and alum-amended poultry litter (PL) indicate that on average 40 ± 14 % of the phosphate in alum-amended PL are bound either as surface complexes on aluminum hydroxide or as an uncondensed aluminum hydroxyphosphate precipitate. In both alum-amended PL and unamended PL, phosphate is present as a calcium phosphate phase, probably a surface precipitate at calcium carbonate surfaces or tribasic calcium phosphate. Only a minor

proportion can be clearly identified as inorganic orthophosphate bound by hydrogen bonds and is expected to be readily water-soluble. A large proportion (= 50 %) of the phosphate species cannot be resolved by ^{31}P -NMR. These species are probably organic and inorganic orthophosphate complexed by a variety of cations in an inhomogeneous environment.

This research demonstrates the scope and limitations of solid-state ^{31}P -NMR spectroscopy for the analysis of heterogeneous materials such as poultry litter. It further provides a basis for the interpretation of solid-state ^{31}P -NMR spectra of other environmental samples, e.g. whole soils or size fractions of soils, composts, sewage sludge, or animal wastes.