

Report for 2002DE4B: Graduate Fellowship in Water Quality: Mechanisms of Phosphorus Stabilization in the Soil Environment: A Molecular Scale Evaluation

- Water Resources Research Institute Reports:
 - Hunger, Stefan., and D. L. Sparks. 2001 and 2002. Mechanisms of Phosphorus Stabilization in the Soil Environment: A Molecular Scale Evaluation. Annual reports to the Delaware Water Resources Center, University of Delaware, Newark, Delaware, 29 and 3 pages, respectively.
- Articles in Refereed Scientific Journals:
 - Hunger, Stefan, H. Cho, J. T. Sims, D.L. Sparks (2003). Direct speciation of phosphorus in alumamended poultry litter: A solidstate ^{31}P NMR investigation, Environmental Science and Technology, in Review.
- Dissertations:
 - Hunger, Stefan. 2003. Mechanisms of Phosphorus Stabilization in the Soil Environment: A Molecular Scale Evaluation. Ph.D. Dissertation, University of Delaware, Newark, DE. 131 pages.

Report Follows:

Basic Information: Fellow Project #3 (of 3)

Title:	Mechanisms of Phosphorus Stabilization in the Soil Environment: A Molecular Scale Evaluation
NIWR Project Number:	2002DE4B
Start Date:	3/1/2000
End Date:	2/28/2003
Funding Source:	104B
Research Category:	Water Quality
Focus Category:	Agriculture (AG), GeoChemical Processes (GEOCHE), Non Point Pollution (NPP), Nutrients (NU), Sediments (SED), Water Quality (WQL)
Descriptors:	Agriculture, Eutrophication, Nutrients, Phosphorus, Runoff, Soil Chemistry, Soil-Water Relationships, Water Quality
Principal Investigators:	Stefan Hunger, University of Delaware PhD candidate
Other Principal Investigators:	Donald L. Sparks dlsparks@udel.edu , Department of Plant and Soil Sciences, University of Delaware, advisor
Project Class:	Research

Previous Project Numbers: DWRC G-01 (FY00); NIWR 2001DE4302B(FY01)

Publications

1. Hunger, Stefan., and D. L. Sparks. 2001 and 2002. Mechanisms of Phosphorus Stabilization in the Soil Environment: A Molecular Scale Evaluation. Annual reports to the Delaware Water Resources Center, University of Delaware, Newark, Delaware, 29 and 3 pages, respectively.
2. Hunger, Stefan, H. Cho, J. T. Sims, D.L. Sparks (2003). Direct speciation of phosphorus in alumamended poultry litter: A solidstate ³¹P NMR investigation, Environmental Science and Technology, in Review.
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The names and degree level (highest level during the reporting period) of all students who worked on the research project is: Stefan Hunger, PhD recipient, June 4, 2003.

A DWRC newsletter article on this project may be found at:
<http://ag.udel.edu/dwrc/newsletters/Page4-Stefan.pdf>

SUMMARY

Background / Justification

In areas of intensive agriculture, eutrophication by nutrients run-off from the fields poses a severe threat to water quality. Phosphorus (P) has been recognized as the limiting nutrient for eutrophication to occur in fresh water and the reactions determining its mobility in soils deserve therefore special

attention. The most common form of P in soils is orthophosphate, either as the free or adsorbed anion, in inorganic mineral phases, or as organic phosphate esters. The most common sources of phosphate in agriculture are commercial, inorganic fertilizers and animal manures, containing mostly organic forms of phosphate. Unfortunately, only limited information exists about the mechanisms of phosphate sorption and desorption reactions in soils or in animal manures. To reduce the amount of water-soluble phosphate in poultry litter (PL), which is produced by confined animal operations on the Delmarva Peninsula and applied to fields locally, chemical amendments such as alum have been applied. Finally, phosphate interacts with a multitude of metals in soils and competes with anions for sorption sites on soil minerals. The sorption reactions of phosphate in soils and similar systems, such as PL, are thus complex. Some degree of knowledge about phosphate sorption reactions can be gained from macroscopic studies by measuring the phosphate uptake from solution by soil minerals and determining its dependence on environmental variables. Although this allows for some level of generalization, no information on the phosphate forms on a molecular level is available from these experiments. To extend the information gained from macroscopic data, one has to combine them with results from spectroscopic investigations. This will allow sound predictions of phosphate mobility and availability in soils or similar systems and help implement useful nutrient management plans.

Solid-state phosphorus nuclear magnetic resonance (NMR) spectroscopy and phosphorus X-ray absorption near edge structure (XANES) spectroscopy have emerged as important spectroscopic tools in the environmental and soils sciences, which allow the investigation of chemical forms of phosphate on a molecular scale. Both methods are suited for the study of phosphate species in soils and PL.

Objectives

The objectives of the research in the past year were to:

1. Investigate phosphate speciation in alum-amended and unamended PL samples using solid-state ^{31}P -NMR spectroscopy as a spectroscopic tool to identify major species and propose a mechanism for phosphate stabilization in alum-amended PL.
2. Investigate phosphate complexes at the gibbsite surface using solid-state ^{31}P -NMR spectroscopy to elucidate the influence of reaction conditions such as time and pH on phosphate speciation. Gibbsite is used as a model aluminum mineral for clay-size aluminum hydroxides and hydroxide coatings on primary minerals in soils.
3. Investigate the cooperative sorption of phosphate and calcium to the gibbsite surface using a combined macroscopic-spectroscopic approach and identify possible reaction mechanisms responsible for the increased sorption of both ions according to the spectroscopic results.

Methods

NMR experiments were conducted at the Environmental Molecular Sciences Laboratory in Richland, WA. XANES experiments were conducted at the National Synchrotron Light Source, which is part of Brookhaven National Laboratory in Upton, NY. Both techniques give information about the local environment of the observed atom and do not require the sample to be crystalline. Both are therefore ideally suited to investigate amorphous or heterogeneous samples such as poultry litter or sorption complexes on mineral surfaces.

The spectroscopic experiments were combined with macroscopic studies. Uptake of phosphate by gibbsite in suspension was investigated under different conditions and in the presence and absence of calcium. The amount of phosphate sorbed to the surface is defined as the amount disappearing from solution, which was measured as the difference between the initial concentration and the concentration after an equilibration time.

Results to date

Calcium phosphate and organic phosphate diesters were identified as principal fractions in both unamended and alum-amended samples. A minor fraction in all samples was inorganic phosphate, probably bound by hydrogen bonds to functional groups in the organic matrix and to adsorbed water molecules. A major fraction of phosphate in the amended samples was adsorbed to amorphous aluminum hydroxide, which forms from alum by hydrolysis of Al after alum addition to the alkaline PL. Aluminum phosphate was detected in minor quantities in two of the alum-amended samples, indicating that it did not play a part in the process of fixing phosphate in alum-amended poultry litter or manure in general. It appears that the hydrolysis of aluminum is kinetically preferred over the formation of aluminum phosphate, although the latter is thermodynamically more stable at the pH values initially reached after the application of alum. This is to our knowledge the first comprehensive qualitative and quantitative investigation of phosphate species in alum-amended poultry litter.

- Results from a solid-state ^{31}P -NMR investigation of phosphate complexes on the gibbsite surface indicate that with increasing reaction time the phosphate speciation changes to a higher coordination number of phosphate with aluminum and therefore to a higher stability. The same effect could be observed with lowering the reaction pH value at constant reaction times.

Results from the combined macroscopic – spectroscopic investigation of phosphate stabilization in the presence of calcium at the gibbsite surface indicate that the mechanism of increased phosphate uptake in the presence of calcium and increased uptake of calcium in the presence of phosphate is not due to the extensive formation of a calcium phosphate phase. Results from different spectroscopic approaches (P-XANES and solid-state ^{31}P -NMR spectroscopy), however, are somewhat contradicting and a more thorough investigation is needed.