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BARD

FINAL REPORT

PROJECT NO. I-461-82

**Sorption and Desorption of Ortho-Phosphate from
Reference and Soil Clay as Influenced by Chemical
Factors Existent Near Plant Roots**

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SORPTION AND DESORPTION OF ORTHO-PHOSPHATE FROM REFERENCE AND SOIL CLAY AS
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Names of Investigators:

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Cooperating Institution(s): Dept. of Soils, U.C. Riverside, Ca, USA.

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Abstract

The effect of citric, formic and tartaric acids and their anions, sodium bicarbonate and amino carboxylate on the adsorption and dissolution of phosphate from soil clay mineral separates and pure clay minerals, was studied. The purpose of that study was to investigate the effect of organic compounds, known to be excreted from roots of various crops, on the reactions of P with surfaces of clay minerals.

It was shown that organic compounds containing one or more OH groups displace adsorbed P from clay particles. Amino compounds increase the affinity of the phosphate to 2:1 clay surfaces, even if they contain OH groups in their molecule. The systematic study of P adsorption as a function of pH, ionic strength and organic ligand concentration have led us to suggest a unified explanation of the phenomena of phosphate adsorption. Maximum P adsorption occurs at pH 5.1 on kaolinite and at pH 6.2 on montmorillonite. These values are very close to the PZC of these clays. At dilute suspension of 2:1 smectite minerals no phosphate interacted with the clay. When the clay collapsed due to high ionic strength or to H-bonding due to amino acid adsorption the broken edges of the mineral expose active aluminum sites that are capable to bind phosphate.

This work has put forward explanations and clarified the mechanism of phosphate binding to clay minerals. The major practical outcome of this research is that it was shown that high salt concentration increases the phosphate binding to the clay.

It suggests that under saline soil conditions higher phosphate application will be needed to supply enough phosphate to plant growth.

3. Objectives and Significance of Research

3.1. Objectives

1. To describe quantitatively the concentration of o-phosphate in aqueous solution, when the conditions for both adsorption and precipitation reactions exist simultaneously, as a function of: pH value, the concentration competing anions, and phosphate-precipitating cations, adsorbing surface characteristics, ionic strength, and the adsorbent-aqueous solution ratio.

2. To study the effects of the above-mentioned factors on the kinetics of adsorption and desorption processes for o-phosphate.

3. To develop and compare reasonably simple, chemically-based models of o-phosphate adsorption and precipitation reactions in the presence of root excretion products.

Description of cooperation

Three phases of cooperation were observed during this study.

- 1) Project preparation. The project was developed and prepared during the period of a sabbatical leave of the principal investigator in U.C. Riverside. Careful planning and sharing of efforts were decided. The Israeli group concentrated on pure clays. The American group concentrated on reactions on clay separates from soil.
- 2) Exchange of ideas and reviewing each other's results during the actual period of work, which resulted in joint publications, that was strengthened by a meeting at Oxford in summer 1984 of the two leaders of this project.
- 3) Final interpretation of the results of the two groups was done during the summer of 1986, during the visit of the principal investigator in Riverside. The unifying principles of phosphate adsorption on clays were formulated in this meeting.

Evaluation of the research achievements

The work followed exactly the outlines specified in the project.

Studies of P adsorption at constant pH values, ionic strength and constant amount of P in the system led us to define the PZCe of Kaolinite at 5.1 and Montmorillonite at 6.9.

The use of carboxylate with and without amino groups at various supporting electrolyte ionic strength has clarified the adsorption model of phosphate on montmorillonitic clays and confined it to the edges of the quasi-crystals of the montmorillonite. It was postulated that increasing the size of the quasi crystal in the c-axis due to increase in the ionic strength or hydrogen bonding of amino groups exposes more active Al^{3+} ions on the clay edges by reducing the spillover of the permanent negative force lines. Phosphate can come in contact with these active Al^{3+} ions since it is not repelled from the quasi crystal side, while it is repelled from a single plate of clay in dilute salt solution.

Chemical compounds that can contribute OH^- to the surface, increase the pH above the pK of the surface or complex Al^{3+} ions, are capable of releasing P from its binding sites on the clay.

It is concluded that root excretions of carbonate or citrate ions can desorb P from clay surfaces while excretion of Amino acids will increase the phosphate binding to montmorillonitic clays. The phosphate desorb from swelling clays at low ionic strength and at high solution to clay ratios. The measurements of water soluble P in the soil should be measured at actual columns of soils at the same density as found in the field.

List of Publications

- 1) Traina, S.J., G. Sposito, D. Hesterberg and U. Kafkafi, 1986.
Effect of pH and Organic Acids on Orthophosphate Solubility
in an Acidic Montmorillonitic Soil. Soil Sci Soc. Amer. J. 50,
45-52.
- 2) Traina, S.J., G. Sposito, D. Heterberg and U. Kafkafi, 1986.
Effect of ionic strength, Calcium and Citrate on Orto-phosphate
Solubility in an Acidic Montmorillonitic Soil. Soil Sci Soc.
Amer. J. 5, 623-627.
- 3) Traina, S.J., G. Sposito, G.r. Bradford and U. Kafkafi, 1987.
Kinetic study of Citrate effects on Orthophosphate Solubility
in an Acidic Montmorillonitic Soil. Submitted for publication.
Soil Sci Soc. Amer. J. 198
- 4) Sposito, G. 1986. On distinguishing adsorption from surface
precipitation. in: "Surface processes in aqueous Geochemistry"
(J.A. Davis and K.F. Hayes, eds.). ACS Symposium Series Am.
Chem. Soc. Washington, D.C., 1986.
- 5) Bar-Yosef, B., U. Kafkafi, Rivka Rosenberg and G. Sposito, 1987.
Competitive adsorption of P on Ca and K-saturated Kaolinite and
Montmorillonite: I. Effect of Equilibration time, Ionic strength,
P concentration and pH. Submitted for publication.
- 6) Kafkafi, U., B. Bar-Yosef, Rivka Rosenberg and G. Sposito, 1987.
Competitive adsorption of phosphate on Ca^+ and K^+ saturated
Kaolinite and Montmorillonite: II. Organic onion competition.
Submitted for publication.