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**Phosphates in suspensions of alkaline, basaltic soils**

**Brito, Jorge Manuel Santos Sousa, Ph.D.**

**The University of Arizona, 1990**

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PHOSPHATES IN SUSPENSIONS  
OF  
ALKALINE, BASALTIC SOILS

by

Jorge Manuel Santos Sousa Brito

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF SOIL AND WATER SCIENCE  
In Partial Fulfillment of the Requirements  
For the Degree of  
DOCTOR OF PHILOSOPHY  
  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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As members of the Final Examination Committee, we certify that we have read  
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entitled Phosphates in Suspensions of Alkaline, Basaltic Soils

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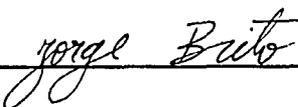
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**DEDICATION**

**To the dearest BRITOs in the World: my parents Hilário and Esther, my son Marcos and my wife Hermengarda.**

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## ABSTRACT

The phosphate solid-solution activities in the A and A<sub>1</sub> horizons of ten alkaline soils from basalt were calculated in order to assess their conformity to solid-solution behavior. Nine soils were from the Cape Verde Islands and one from Arizona. Four of the Cape Verdean soils belonged to the same series (Ponta) but presented different levels of P fertilization. The other soils were not fertilized. All soils behaved in conformity with solid-solution theory. Three assumptions were made: 1) Surfaces of minerals are similar because of weathering; 2) Partial equilibrium was reached; 3) The mole fraction of the total solid composition is similar to the X of the surface of the solid.

A preliminary test was conducted for optimization of experimental conditions, which turned out to be: 24-25°C; 1:5 soil solution ratio; 0.01M CaCl<sub>2</sub> extracting solutions. The relation of pH vs. time was used as the indicator of change and suspensions were kept for 21 days until pH stabilization. After filtration, electrical conductivity, soluble Ca, Mg and P were measured. A second experiment was done on selected samples, in order to study the influence of added Ca on the Solid Activity Coefficient (SAC). SAC and ionic solid activity coefficients for phosphates were computed from the data and the equation  $IAP = g \times K_{sp}$ . K<sub>sp</sub> of different Ca phosphates were taken as reference. Best results were found with octocalcium phosphate and bobierite as reference for calcium and magnesium phosphates respectively.

The curves of  $\log \text{SAC}$  vs.  $P_{\text{added}}$  were linear, indicating confirmation of solid solution behavior. Fertilized and virgin soils presented different slopes for those curves. Based on octocalcium phosphate, the basaltic soils yielded phosphate ionic solubility coefficients on the range 1 to 4 which are very low compared with similar coefficients calculated in the literature for non basaltic soils. The amorphous nature of basaltic minerals was considered as an explanation for the solid-solution behavior observed.

Results show reasonable conditions for magnesium phosphate formation and no influence of added Ca on the linearity of  $\log \text{SAC}$  vs.  $P_{\text{added}}$  plots. However Ca levels corresponding to I.S. around 0.028 produced a considerable drop on the values of SAC when bobierrite was taken as reference.

## INTRODUCTION

With this work it is my intention to give a modest contribution to soil science as well as to the development of agriculture in my country: Cape Verde Islands.

Cape Verde is a small volcanic archipelago located in the sahelean climatic zone, about 400 miles west of the continent of Africa. Santiago is the largest of the ten islands and one with the most irrigated areas, thus, with higher demand for plant's macronutrients, namely phosphorus.

### Scope of the Dissertation

Phosphates contain one of the three major macronutrients for plants: phosphorus (P). It is a common component of chemical fertilizers, likely because its availability to plants in most soils is very low.

It is well known, that when water-soluble phosphate compounds are added to soils, considerable proportion of P becomes insoluble, hence unavailable to plants within a few hours (Ford 1933; Moser 1942, Devis 1943).

The nature and characteristics of this behavior has long been concern for scientists, who have proposed different and sometimes conflicting theories for explaining and quantifying such decrease in phosphate solubility.

Most soil scientists state that phosphorus retention involves both absorption and precipitation reactions. However the contribution they

attribute to each of these reactions differs. In addition, results have been unsatisfactory and a common ground of interpretation is yet to be found.

For these and other reasons, different schools have evolved through the years, with different approaches:

1) Emphasis on Adsorption

Adsorption seems to be considered the main reaction over a short period (Griffin and Jurinak 1973; Rajan and Watkinson 1976). Consequently adsorption has been studied by a very large number of researchers.

The Langmuir equation (Langmuir 1918) has been frequently applied to these studies. New forms of that equation have been used as well as other adsorption equations. In general the results are graphically expressed as sorption isotherms.

2) Emphasis on Precipitation

Another group of scientists looked at the problem under the precipitation dissolution prism. Thermodynamic concepts like solubility product ( $K_{sp}$ ) and ionic activity products (IAP) are often utilized and results expressed graphically as solubility diagrams.

Among those scientists the name of Lindsay stands out. (Willard L. Lindsay - centennial Professor of Colorado State University, Fort Collins).

3) The Solid Solution Concept

Recently, some researchers started to consider the solid solution concept which takes into account adsorption and precipitation but a different approach.

Among scientists advocating this concept , two groups are most visible: the Blanchar group (R.W. Blanchar - Professor of Agronomy, University of Missouri Columbia, MO 65211) and the Bohn group (Hinrich L. Bohn Department of Soil and Water Science, University of Arizona, Tucson Arizona 85721).

The former group considers in their computations only the phosphorus coming from the surface of soil solid particles whereas the latter uses the total P content of the soil.

Both groups have been working with acid soils; alkaline soils would probably present some additional problems and it is the intention of the Bohn group to undergo such studies. As a graduate student in the Bohn group, I have opted for considering such studies as the basis for my dissertation.

Since phosphates are important to Cape Verdean Agriculture and most of the country's soils are alkaline, this type of solid activity studies can be done with Cape Verdean soils. Alkaline soils may be originated by  $\text{CaCO}_3$  precipitation or from basic parent materials like basalt (or both). Alkaline soils in Cape Verde are mostly basaltic.

Since the problem of isolating the "true" soil solution has not yet been solved (Sposito, 1986), several other methods have been established as compromises between analytical convenience and chemical accuracy (Amacher, 1984); among them, the use of aqueous suspensions is the most convenient.

For the reasons stated above this Dissertation will be:

- focusing on: phosphates in suspensions of alkaline, basaltic soils
- using: Cape Verdean soils (90% of the soils used)
- considering: the solid-solution theories (with total P measured) as its main theoretical approach.

#### Statement of Objectives

Taking all previous considerations into account, the main goals of this research are:

1) Evaluating the solid solution concepts for interpreting salt solid activity coefficients of calcium and magnesium phosphates obtained when considering the influence of:

- Not adding phosphates to the suspensions
- Adding increasing amounts of phosphates to the suspensions
- Ca and Mg activities with fixed added Ca
- Ca and Mg activities with variable added Ca

2) Calculate the ionic solid activity coefficient of  $\text{PO}_4^{3-}$  on the above situations.

3) Consider other approaches related to the solid solution treatment.

## REVIEW OF THE LITERATURE

As noted in the Introduction, the P-retention problem caught the attention of researchers in the early thirties and has since been, the subject of different approaches and explanatory theories in the scientific community.

Researchers with physical thermodynamic inclinations have been putting their energies on the study of P adsorption reactions, whereas those preferring chemical thermodynamics have studied P precipitation reactions. More recently some of them are considering the solid solution approach.

### Phosphorus Retained by Adsorption Mechanisms

#### Initial Studies

Once the P-retention occurrence referred to by Ford (1933) Moser (1942) and Davis (1943), was followed by the identification of the main constituents responsible for such retention by Black (1943), Coleman (1945) Kittrick and Jackson (1955a) on acid soils. They identified Al and Fe, either present in the free oxide forms or available through dissolution of clay minerals, as the responsible agents.

Methods of measurement of phosphate adsorption capacity in acid soils were proposed by Bass and Sieling (1950), Dean and Rubins (1947) and Piper (1947).

Since adsorption isotherms had been successful in describing gaseous adsorption on solids, some authors started used them to describe ion adsorption by soils.

#### Langmuir Equation and Soils

The Freundlich equation (Freundlich 1926) was one of the first adsorption isotherms used to describe phosphorus adsorption in soils (Davis 1935; Rurtz et al. 1946; Low and Black 1950; Russel 1954). However, Olsen and Watanabe (1957) pointed out that the Freundlich equation presented some limitations such as the inability to determine an adsorption maximum and the applicability only to large amounts of adsorbed P. Instead they used the Langmuir equation (Langmuir 1918) which did not present such limitations.

This was the first time that the Langmuir theory for gas adsorption onto solids was applied to phosphate sorption in soils. It became the most widely applied adsorption equation by soil scientists.

The initial derivation of the equation was based on the following assumptions: 1) The adsorbed species is bound to the surface at homogeneous, specific sites, forming a monolayer; 2) The heat of adsorption is constant over the entire monolayer and does not depend on the extent of the surface coverage; 3) There is no lateral interaction between adsorbate molecules; 4) Equilibrium is attained; 5) The constants in the equation are independent of the temperature. (Bohn et al. 1985, White and Zelazny 1986). Because of later revisions to the assumptions, this equation is now known as the one-site Langmuir equation (White and Zelazny 1986). The equation has been linearized under many

forms allowing the determination of its two constants from the plots: one is related to the heat of adsorption and the other is the maximum amount of adsorbate that can be adsorbed (the adsorption maximum). The most used of the linearized forms of the Langmuir equation predicts a straight line when equilibrium concentrations of adsorbate are plotted against the ratio between such concentrations and the amount of adsorbate fixed per unit of adsorbent. However these plots are often curvilinear when applied to soils (Olsen and Watanabe, 1957; Gunary 1970; Udo and Uzu, 1972; Griffin and Jurinak, 1973b; Holford et al., 1974; Taylor and Ellis, 1978).

In order to cope with this problem, alternative approaches were made:

- Olsen and Watanabe (1957) as well as Rennie and McKercher (1959) discarded the curvilinear part of the plot corresponding to high P concentration and considered that the Langmuir equation was only obeyed at low P concentrations.

- Other researchers resolved the curvilinear line into two slopes indicating at least two different populations of sites for the same P adsorption mechanism. (Syers et al. 1973) or two adsorption mechanisms (Harter, 1968; Shuman, 1975) for the same population of sites.

- Rãjan and Watkinson, (1976) resolved the curvilinear line into more than two slopes and Gunary (1970) added a square root term to the Langmuir equation.

The failure to obey a linear Langmuir equation got several explanations, based on the breach of the original assumptions:

1) Griffin and Jurinak, (1973b) and Muljadi et al., (1966) described reactions which might be responsible for:

- i) adsorption occurring at different sites on the surface.
- ii) adsorption taking place in layers on the surface.
- iii) separate mineral species being nucleated on the surface.

2) Bache and Williams (1971) reasoned that the deviations were due to sorbed P migrating into the surface layers.

3) Adamson (1967) and Clark (1970) suggested that the surface heterogeneity and increasing interactions between adsorbate molecules and surface coverage were responsible for variations in heat of adsorption.

4) Many researchers found P-adsorption to be endothermic: Low and Black (1950) on kaolinite; Griffin and Jurinak (1973b) on  $\text{CaCO}_3$ ; Kuo and Lotse (1974) on lake sediments; Taylor and Ellis (1978) on Dowex I-X8; and Mehadi and Taylor (1988) on highly weathered soils. As endothermic, means adsorption of energy, it is natural that some researchers attributed the curvature in Langmuir plots to heterogeneous adsorption energies of the minerals (Lin et al.1983).

#### Multi-Site Adsorption.

As seen, the early forms of the Langmuir equation generally give curvilinear plots when applied to soils.

White and Zelazny (1986) summarized the problems with the application of the original one-site Langmuir equation as follows:

1) Inability to distinguish between adsorption and other reaction mechanisms (Veith and Sposito, 1977).

2) Failure to be linear when certain levels of adsorbate concentration are needed for fixation.

3) Inability to apply to heterogeneous surfaces (Sposito 1982, Syers et al 1973).

4) Incapability to take coupled adsorption-desorption reactions into account (Harter and Baker 1977, 1978).

A multi-site Langmuir equation was then proposed by Syers et al. 1973, based on non-uniformity of site populations. However, despite solving the problem of heterogeneous sites, this equation still does not consider lateral interactions, assumes constant heat of adsorption and does not address the problem of coupled adsorption-desorption phenomena.

In order to account for these coupled adsorption-desorption reactions, Harter and Baker (1977, 1978) applied correction factors to the single and multi-site Langmuir equations. A theoretical treatment by Sposito (1982) showed that these adsorption-desorption Langmuir equations are correct only if there has been no previous adsorption of the studied ion. This suggests a better fit of the equation for virgin or non fertilized soils; indeed Mehadi and Taylor (1988) obtained a better fit of the points for virgin soils when their data were plotted using the Langmuir equation modified by Harter and Baker (1977).

### Variable Heat of Adsorption

Many times, when data fail to conform to the Langmuir equation, the Freundlich equation is used, which often gives best results, especially if working with low surface coverage.

The Freundlich equation was derived to permit a logarithmic decrease in the heat of adsorption with increasing coverage, whereas the Langmuir equation implies that the heat of adsorption is independent of surface coverage. Both consider monolayer adsorption at specific sites.

Low and Black (1950) used a modified form of the Freundlich equation and found a better fit to their data. Fitter and Sutton (1975) added a term to the Low and Black equation in order to account for P already present in the soil. They found better results with the modified equation than with the Langmuir equation.

Shaviv and Shackar (1989) and Shaviv et al (1989) used the Freundlich equation to fit their data and to derive a kinetic-mechanistic model for phosphorus sorption.

The Freundlich equation has received some criticism: Bohn et al. (1985) consider that the frequent good fit of data is influenced by the "insensitivity of log-log plots" and by the flexibility for curve fitting of the two empirical constants in the Freundlich equation. The objections of Olsen and Watanabe (1957) are still relevant: no prediction of adsorption maximum and limitation only to low amounts of adsorbed P.

Another isotherm, the Temkin equation, assuming a linear rather than logarithmic decrease of the adsorption energy, was used by Bache and Williams (1971) but gave nonlinear plots.

### Multilayer Adsorption

The possibility of multilayer adsorption in soils was first addressed by Griffin and Jurinak (1973b) who used the BET equation (Brunauer, Emmett and Teller. 1938). This equation does not assume monolayer adsorption but still ignores lateral interactions and assumes homogeneous surfaces.

Griffin and Jurinak (1973b) found that the break between the two lines in a two-site Langmuir equation plot corresponded to a change from undersaturation to oversaturation, concerning octocalcium phosphate. In addition, the adsorption maxima calculated by BET and from the first line of the Langmuir plot were very close.

This change of saturation status is taken into account in the BET equation through a term representing the concentration of the adsorbed species required to precipitate the most probable solid form of such species.

Taylor and Ellis (1978) and Mehadi and Taylor (1988) also found good agreement between the two-site Langmuir and the BET equations but consider the break as corresponding to a change from two-point to one-point bonding of P.

### Phosphorus Retained by Precipitation Mechanisms

Naturally, the first idea coming to mind when the concentration of a salt decreases in a solution, is to look for precipitation reactions. In order to do so, thermodynamic criteria has to be applied, the species

involved have to be identified and solubility data on those species should be reliable.

When it comes to P precipitation in soils, the task becomes very complicated because: 1) several different P compounds may be present in the soil; 2) different soil phases participate in the reactions; 3) solubility data on each of the identified compounds have to be determined and to be reliable; 4) P reactions are very slow and the application of thermodynamic criteria asks for equilibrium establishment.

According to Lindsay and Moreno (1960), the kind of considerations just made are the reason for the limited attention being received by a thermodynamic interpretation of phosphate reactions, since the theoretical treatment by Buehrer (1932) of phosphate reactions in calcareous soils.

Based on the advances obtained, as referred to above, Lindsay and Moreno (1960) were prompted to pursue the thermodynamic approach.

These advances obey the following experimental path: the possibility of P compounds precipitation led researchers to conceive experiments which allowed the application of the solubility product principle. As a result, evidence of crystalline phase precipitation was presented and the identification of P compounds in such phases was facilitated. The determination of solubility data on these minerals followed, which in return provided more accurate data for a better application of the solubility product principle.

## Solubility Product and Soil P

Low and Black (1948) were among the first to explain phosphate reactions in soils under the solubility product principle criteria in which they carried out kaolinite dissolution experiments and obtained the precipitation of an aluminum phosphate.

One year later, Swenson et al. (1949) observed that certain anions which were able to complex Fe and Al, were also able to release P from soil. These reactions were quantified by Struthers and Sieling (1950).

Kittrick and Jackson (1955b) applied solubility product criteria to evaluate qualitatively Al and Fe phosphates related to kaolinite-variscite systems. Quantitative determination of the phosphate content of the solution phase were done by these authors (1955c) and by Hemwall (1957) in similar experiments.

Clark and Peech (1955) and Aslyng (1954) measured the phosphate content in soil extracts and were able to relate the findings to the solubility of calcium phosphates. Lindsay et al. (1959) did the same with acid soils and found correlation with the solubility of variscite.

## P in Precipitated Phases

Kittrick and Jackson (1955a) by electron microscopic observation were able to present evidence of crystalline phase formation when phosphate solutions were put in contact with soil minerals.

Lindsay and Stephenson (1959) studied the fate of monocalcium phosphate monohydrate in soils and found out

that Al and Fe would dissolve and reprecipitate under new crystalline forms. In addition they found that a dicalcium phosphate dihydrate precipitation would also take place.

Wada (1959) reacted ammonium phosphate with soil minerals and presented evidence of ammonium taranakite formation.

Haseman et al. (1950, 1951) by reacting phosphate solutions with clay minerals and iron and aluminum oxides, were able of demonstrating precipitation of complex new crystalline phosphates.

The following calcium phosphates were identified in soils by Lehr and Brown (1958) and Lehr et al. (1959) once the soils reacted with superphosphate: 1) dicalcium phosphate anhydrous; 2) apatite; 3) dicalcium phosphate dihydrate; 4) octocalcium phosphate. The solubilities of the last two were determined by Moreno et al. (1960a, 1960b).

#### Solubility Diagrams

The thermodynamic approach of Lindsay and Moreno consisted of the use of more accurate solubility data to develop phosphate solubility diagrams for soils (Lindsay and Moreno 1960).

These solubility diagrams plotted the negative log of  $H_2PO_4$  ion activity against the pH for different phosphate minerals. These plots were lines representing the activity solubility isotherms for different phosphate compounds.

The usefulness of these diagrams is that they permit the determination of the relative stabilities of phosphate compounds at various pH values: 1) the precipitation of a compound is possible if the

$\text{pH}_2\text{PO}_4$  value is above the respective isotherm, meaning that the soil solution is supersaturated with respect to that compound; 2) conversely if  $\text{pH}_2\text{PO}_4$  falls below the isotherm, we should expect the dissolution of the compound (if present). (Lindsay and Moreno 1960).

Solubility diagrams became popular since then, and were used for all kinds of minerals. Lindsay (1979) published a book, *Chemical Equilibria in Soils*, where emphasis is placed on minerals and solid phases under the solubility product criteria; minerals are grouped by their cationic components (except carbonates and phosphates) and the solubility diagrams are presented as log of ion activity vs. pH. This book is the result of 20 years of research and is also the compilation of the most accurate solubility data available at the time. Most of the subsequent literature on the subject has been using solubility data from this source.

Despite all this progress, soil solution concentrations of most ions are lower than the ones predicted by solubility data and diagrams for the mineral solid phases (Hendrickson and Corey 1981).

#### P Retained by Solid-Solution Formation Mechanisms

##### A Better Approach is Needed

It seems clear that neither adsorption nor precipitation mechanisms explain completely the phenomena of P retention by soils.

Even though scientists favor one mechanism over the other, no one denies the mixed nature of the phenomena. However the way each researcher sees this mixed nature may differ as they consider:

### 1) Conditions dictating which mechanism prevails

As referred by Lin et al. (1983) many investigators consider that adsorption mechanisms prevail at low P concentrations whereas precipitation mechanisms occur at high P concentrations.

### 2) Coexistence of the mechanisms

Larsen (1967) considers phosphate sorption as an equilibrium between soluble, adsorbed and precipitated phosphates.

The BET equation seems to address both mechanisms. However the main criticism of the equation is that the term representing the concentration needed for precipitation to take place, limits the usage of the BET equation in soils. The reason for the limitation is because it is difficult to choose such a term when many solid forms can precipitate (White and Zelazny 1986).

### 3) Different interpretations of the same phenomenon

Lin et al. (1983) thought both reactions resulted from the same chemical force.

Veith and Sposito (1977) have shown that complex precipitation reactions can also exhibit adsorption behavior, hence, they are construed as anionic adsorption.

## The Use of Solid-Solution Concepts

The more comprehensive approach appears to be the incorporation of solid-solution concepts to the solubility theory.

The fact that the ion activity product (IAP) of a component in the soil solution is less than its corresponding solubility product ( $K_{sp}$ ) as pointed out by Hendrickson and Corey (1981), made researchers

pay more attention to the activity of the solid phase, which until then had been considered as unity.

Bohn (1981) manifested the need for identification of the mole fraction of components in solid phases, as a means of calculating the solid-phase activity.

Blanchar and Stearman (1984) combined ion product concepts with estimates of P solid-phase activity in order to predict P solubility as a function of retained P (Blanchar and Stearman, 1985). By so doing, they were able to calculate phosphate solubilities close to measured ones.

#### Solid-Solution Theory and Soils

The framework of the following solid-solution theory was gathered, along with most of the references, from the work of H.L. Bohn (Bohn and Bohn, 1987; Bohn, 1990) as summarized next:

Bohn (1990) defines solid-solution as "homogeneous or regular (nearly homogeneous) mixtures and coprecipitates of two or more solids in the same crystal lattice or glass", and considers isomorphous substitution of small amounts of ions into a crystal also as a solid-solution.

Studies showed that such mixing decreases the chemical potential and solubility of each component in the mixture relative to the chemical potential and solubility of the same component in its pure state. Those studies also make analogies with the evaporation of liquid mixtures (Gressens 1981b; Babcock and Doner 1981).

The chemical potential (considered as a measurement of the escaping tendency) of a component in a homogeneous solid mixture is, as in

a gas-liquid mixture, given by (Vaslow and Boyd, 1952; McIntire 1963; Crockett and Winchester, 1966; and Thorstenson and Plummer 1977).

$$\mu_1 = \mu_1^\circ + RT \ln g_1 X_1 \quad (1)$$

Where  $\mu_1^\circ$  represents the chemical activity of the component in the pure solid,  $X_1$  its mole fraction and  $g_1$  its activity coefficient. The term  $RT \ln X_1$  represents the entropy of mixing. Thus, a component in a mixture bears more entropy than in a pure state; this leaves less entropy to be gained by the component when going into the aqueous solution, and explains the decrease in solubility.

Another explanation is based on probabilities: the probability of an ion going from the solid into aqueous solution is proportional to its concentration near the solid surface. Thus, it is obvious that in a mixture, this concentration would only decrease since the pure solid represents the maximum concentration possible for the component.

The fact that activities of ions in the soil solution have been found to be less than expected by solubility product calculations (based on pure mineral phases) and the above considerations, made researchers consider the possibility of soil minerals behaving like solid-solutions.

In order to apply solid-solution theory to soil minerals, researchers came up with the following equation

$$IAP = g \times K_{sp} \quad (2)$$

● IAP is the Ionic Activity Product - product of the activities of the solid's ions in the aqueous solution

- $a_g$  (will be referred in this work also as SAC ) is the activity coefficient of the solid, accounting for enthalpy changes (Denbigh 1971)
- $X$  is the mole fraction and the entropy term
- $K_{sp}$  is the solubility product of the pure solid

The above equation may be derived from the referred chemical potential equation (Wright and Peech 1960, Murrman and Peech 1968) or in a more elegant way (Bohn, 1990) by using the ratio between activity expressions giving the aqueous solubility of a component in a pure solid state, and activity expressions representing the aqueous solubility of the component in a solid solution.

Thorstenson and Plummer (1977) found out that equations (1) and (2) were rigorous only if applied to completely homogeneous solid solutions. A completely homogeneous solid solution means that all of its components are equally soluble. This is not the case in soils where incongruent dissolutions take place, leading to changes in the composition of the surface in relation to the interior of the solid particle. This inhomogeneity prevents equilibrium (Gressens 1981a).

Bohn and Bohn (1987) state that homogeneity is a relative concept and argue that the "realistic question is whether and when soils are homogeneous enough to justify Eqs.(1) and (2), i.e., whether soils reach partial equilibrium". Bohn (1990) goes on saying that for weakly-soluble ions in soils, the inhomogeneity and the deviation of total equilibrium "may be of little significance".

Partial equilibrium was defined by Helgeson (1968) through three conditions: 1) one or more components are at equilibrium across a phase boundary; 2) one phase is at internal disequilibrium, and 3) the rate of change of that phase is negligible (in Bohn and Bohn 1987).

Bohn (1990) thinks that those conditions may apply to solid solution in soils, and states that cation exchange and adsorption studies have been tacitly admitting the same assumption.

Another source of arbitrariness in the application of equation (2) to soils is the definition and evaluation of the solid concentration term X.

Blanchar and Stearman (1984, 1985) consider only the soil surface as the controlling phase; they used the ratio between the phosphate sorbed and the Langmuir adsorption maximum as the mole fraction.

Bohn and Bohn (1987) consider, on the other hand, a mole fraction calculated from the total soil composition (Bohn, 1982) as the most convenient choice, since different methods of measuring surface composition have produced different results.

In sum, Eq. (2) appears to be of great value in this new approach if the following assumptions are considered: 1) Enough degree of homogeneity; 2) Partial equilibrium conditions are met; 3) The total soil composition is used on the computation of the mole fraction.

## MATERIALS AND METHODS

### Description of Soils

The samples used in this study are from alkaline soils formed from basaltic parent materials.

Nine samples were taken from two different sites in Santiago, the largest of the Cape Verde Islands.

The first site is the Chão Bom Experimental Irrigation Area, near the town of Tarrafal, detailed characterization of soils has been conducted by scientists and technicians of the Cape Verdean National Institute of Agrarian Research (INIA).

The second site is the state farm of Justino Lopes and nearby non cultivated terrain.

In order to have sufficient and readily available soil for performing preliminary tests, a tenth sample was collected at a University of Arizona property on the Tumamoc Hill in Tucson.

All samples were taken from A and Ap horizons, air dried, passed through a 2 mm sieve and stored in plastic containers prior to use.

Table 1 lists general characteristics of the ten studied soils.

### Experiments

#### Conditions

##### a) Fixed Parameters

A preliminary experiment was conducted in order to assess the best conditions for the establishment of the partial equilibrium defined before. Soil W, the local soil, was used and the following variables were

chosen: duration, ionic strength (0, 0.01, 0.03, 0.10, 0.30) and soil-solution ratio (1:1, 1:2, 1:5). The measurement of pH with time was the indicator of change.

Appropriate amounts of soil were mixed with corresponding amounts of distilled water (Ionic Strength slightly  $> 0.00$  because of soluble salts in the soil) or electrolyte (for higher ionic strengths) to make up the different soil-solution ratios. These suspensions were kept in plastic bottles and shaken every day for 2 minutes. All suspensions were done in triplicate.

According to the results of this experiment (Table 2) and taking into consideration some data from the literature, the following set of conditions was adopted:

- 1) Duration = 21 days

The pH decreased with time in all suspensions. The rate of decrease slowed down after the tenth day and the pH stabilized after 16 days. Previous work has shown that pH and P concentration were constant after 16 days (Blanchar and Stearman 1984, 1985). However recent kinetic studies of phosphate sorption in calcareous soils considered 21 days as a more reliable duration for such experiments (Shaviv and Shachar 1989) 2)

Ionic Strength = 0.03

Phosphate reaction in soils are affected by Ionic Strength among other factors (Bar-yosef et al 1988). Therefore, in order to decrease the number of influencing factors, the ionic strength had to be fixed by means of adding an appropriate amount of an electrolyte to the solution.

Table 1: The Studled Soils and Their Locations

Soil	Texture	Description	Location
T1	Porta loam	Torrifluventic Haplustoll, loamy-skeletal, isohyperthermic	Tarratal (C.V.)
T2	Porta loam	Torrifluventic Haplustoll, loamy-skeletal, isohyperthermic	Tarratal (C.V.)
T3	Porta loam	Torrifluventic Haplustoll, loamy-skeletal, isohyperthermic	Tarratal (C.V.)
T5	Porta loam	Torrifluventic Haplustoll, loamy-skeletal, isohyperthermic	Tarratal (C.V.)
T8	Acacia clay loam	Torrifluventic Haplustoll, clayey, isohyperthermic	Tarratal (C.V.)
A	=== loam	Torrifluent	Justino Lopes (C.V.)
B	=== silt loam	Torrifluent	Justino Lopes (C.V.)
C	=== silt loam	Torrifluent	Justino Lopes (C.V.)
D	=== silt loam	Torrifluent	Justino Lopes (C.V.)
W	Lehmane clay loam	Lithic Haplargid, fine, mixed, thermic	Tumamoc Hill (U.S.)

Source (for Cape Verdean soils) : Southard and Queiroz (1982)

Table 2 : Preliminary Experiment

	Day	Ionic Strength														
		0.00			0.01			0.03			0.10			0.30		
		Soil Solution Ratio			Soil Solution Ratio			Soil Solution Ratio			Soil Solution Ratio			Soil Solution Ratio		
		1:5	1:2	1:1	1:5	1:2	1:1	1:5	1:2	1:1	1:5	1:2	1:1	1:5	1:2	1:1
pH	1	8.6	8.4	8.3	8.1	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3
	2	8.4	8.2	8.1	8.0	7.8	7.7	7.6	7.7	7.7	7.5	7.5	7.5	7.3	7.3	7.3
	4	8.2	8.1	8.0	7.9	7.7	7.6	7.5	7.5	7.5	7.5	7.4	7.3	7.2	7.2	7.2
	6	7.9	7.9	7.8	7.8	7.7	7.6	7.4	7.4	7.5	7.3	7.3	7.3	7.2	7.2	7.2
	8	7.7	7.7	7.6	7.8	7.7	7.5	7.4	7.4	7.4	7.3	7.3	7.3	7.1	7.1	7.1
	10	7.6	7.5	7.4	7.5	7.5	7.4	7.4	7.4	7.4	7.2	7.2	7.2	7.1	7.1	7.1
	12	7.5	7.5	7.3	7.4	7.4	7.2	7.3	7.3	7.3	7.1	7.1	7.1	7.0	7.0	7.0
	14	7.4	7.3	7.1	7.4	7.4	7.2	7.2	7.2	7.2	7.1	7.1	7.1	7.0	7.0	7.0
	16	7.4	7.2	7.1	7.3	7.2	7.1	7.2	7.2	7.2	7.1	7.1	7.1	7.0	7.0	7.0

The preliminary experiment showed no pH variability among the different soil-solution ratio suspensions, when the ionic strength was higher than 0.03.

### 3) Electrolyte = $\text{CaCl}_2$

Calcium chloride was the electrolyte of choice, especially when pH measurements are involved;  $\text{CaCl}_2$  releases  $\text{Ca}^{2+}$  which causes flocculation of clays, hence, a better separation of solution and soil phase. This improves the pH measurement by decreasing the liquid junction-potential error (Coleman & Thomas 1967).

pH measured in 0.01M  $\text{CaCl}_2$  has been recommended as a good approximation of field pH. (Schofield & Taylor 1955; Graham 1959; Woodruff 1967)

A divalent cation with a concentration of 0.01M represents a value of 0.03 for the Ionic Strength, according to the equation  $I=3C$ , which is obtained from the following equation (in Freiser and Fernando 1979) when making  $z^+ = 2$ ,  $z^- = -1$ , the cation concentration = C and the concentration of the anion=2C :

$$I = \frac{1}{2} [C_{M^+} \times (z^+)^2 + C_{M^-} \times (z^-)^2] \quad (3)$$

### 4) Soil-Solution Ratio = 1:5

High ratios are probably better in theory but low ratios are much more convenient.

Since there were no difference among pH<sub>e</sub> of different soil solution ratios at ionic strengths higher than 0.03 the 1:5 ratio was chosen as the most convenient: it is easier to separate the solution phase from the soil phase.

5) Temperature =  $24 \pm 1^\circ\text{C}$

The temperature of the room was  $24 \pm 1^\circ\text{C}$ . This temperature is very close to the standard  $25^\circ\text{C}$  which is convenient for the direct use of equilibrium constants found in the literature.

b) Optimization of Experimental Conditions

Better measurements of ion solubility depend on the state of the surface of the soil solid particles (Bartlett, 1980). Leggett and Argyle (1983) pointed out the need for minimizing changes and effects of previous history of the soil samples on such surfaces.

On that basis the following procedures were followed:

- Samples were not oven dried. Instead their moisture contents were used to determine air-dry weights corresponding to the oven-dry weights needed for the establishment of the soil solution ratios.

- Complexing ligands were avoided and a soil solution ratio higher than the 1:10 generally used in previous work, was adopted.

- Dilution of the major cations was avoided through  $\text{Ca}^{2+}$  addition.

- All measurements were done after the burst of microbial activity had passed.

## Procedures

### a) Main Experiment

Weighed amounts (equivalent to 10g of oven dried samples) of the air-dried 2 mm sieved soil samples, and 50 ml of 0.01M  $\text{CaCl}_2$  solutions containing 0, 25, 50, 100 and 200 mg of P (from  $\text{KH}_2\text{PO}_4$ ) per kg of soil, were added to 125 ml plastic bottles, which were shaken for 2 min every day at room temperature. pH was monitored as indicator of partial equilibrium attainment.

Electrical conductivity measurements were taken on the 1st and last day of soil-solution contact.

After 21 days, the suspensions were filtered through Whatman 42 filter paper and the solution phases kept in 30 ml plastic vials for P, Ca and Mg determinations.

### b) Complementary Experiment

After completion of the main experiment a second experiment was performed was place for the following reasons:

- 1) Precision: confirmation of the results by repeating experimental procedures and analyses on pertinent samples.
- 2) Experimental: study how different concentrations of  $\text{CaCl}_2$  influence the results.

The experimental procedure was exactly the same for the main experiment except for the following:

- 1) Only 0, 100 and 200 mg of P per kg of soil were considered
- 2) The  $\text{CaCl}_2$  concentrations of solutions were: 0.000, 0.003, 0.010 and 0.025 M

- 3) Only soils T<sub>3</sub>, T<sub>8</sub>, A and W were tested
- 4) E.C. measured only on the solution phase after filtering

#### Preparation of Solutions

##### a) For the Main Experiment

Each soil received five treatments. Suspensions were made with five levels of P in 0.01M CaCl<sub>2</sub> solutions as follows:

0, 5, 10, 20 and 40 ml of 1,000 ppm P stock solution were mixed in a volumetric flask with 10 ml of 1.0M CaCl<sub>2</sub> stock solution and completed to 1 L with deionized water. These made 0, 5, 10, 20 and 40 mg P/L solutions corresponding in a 1:5 soil solution ratio, to 0, 25, 50, 100 and 200 mg P/kg of soil, respectively.

The P stock solution was prepared by dissolving 4.4g of KH<sub>2</sub>PO<sub>4</sub> (F.W. = 136.1) in 1 L of deionized water.

##### b) For the Complementary Experiment

Each of the four selected soils received 12 treatments (4 levels of Ca x 3 levels of P). Appropriate amounts of the stock solutions prepared for the main experiment were taken to prepare the 12 combinations.

Prepared levels of Ca were 0, 0.003, 0.010 and 0.025M of CaCl<sub>2</sub> whereas the levels of P were 0, 20 and 40 ppm of P (0, 100 and 200 mg/kg soil).

Later checking of the Ca (by A.A.) and P contents of the prepared solutions confirmed the P levels but showed the 0.025M CaCl<sub>2</sub> to be 0.024M and 0.010M to be 0.009M.

### Analytical Determinations

#### a) pH

The pH meter was a Beckman 21 with automatic temperature compensation. A glass electrode and a reference electrode were used; in order to minimize the liquid junction-potential effect, the glass electrode was immersed in the sediment phase and the reference electrode in the supernatant phase. The pH meter was calibrated with 2 buffer solutions, for better results and accuracy.

#### b) Electrical Conductivity

The conductivity meter used was digital, with auto calibrating resistance, providing direct readouts in dS/m (when chosen).

#### c) Soluble P

Soluble P was determined by the Murphy and Riley (1962) procedure.

The spectrophotometer used was a Bausch & Lomb model 21 and the wavelength was 880 nm.

The calibration curve was linear and obeyed the following linear equation:

$$(\text{ppm of P}) = - 0.0002 + 1.415 \text{ Absorbance} \quad (4)$$

with a regression coefficient  $r = 0.9993$

#### d) Soluble Ca and Mg

These cations were determined by Atomic Absorption in solutions containing  $\text{SrCl}_2$  as an ionization suppressant and refractory releasing agent.

An IL video 12 Atomic Absorption Spectrophotometer was used as a single channel, double beam instrument.

The results were the average of 4 measurements.

The calibration curves were linear and based on 5 points.

e) Total P

Total P in the soil samples was determined following  $\text{HNO}_3$  -  $\text{HClO}_4$  digestion (Olsen and Dean 1965).

Soil samples were crushed in order to increase the surface of contact and oven dried for 24h. 2.0g of each were taken, put in 250 ml Erlenmeyer flasks, on a hot plate and attacked by 25 ml of concentrated  $\text{HNO}_3$  for 30 min followed by 30 ml of 60%  $\text{HClO}_4$  for an additional 30 min.

P determination was carried out by the same photometric procedure as for the soluble P.

## RESULTS

### Data Treatment

#### Experimental Data

##### 1) pH vs. time

For each suspension, three pH readings were taken at a time and the obtained averages are listed in Tables 3 and 4.

The pH decreased from the 1<sup>st</sup> day on, in every suspension. The rate of decrease slowed down by the 8<sup>th</sup> day and reached a steady state by the 18<sup>th</sup> day.

Increasing amounts of phosphate do not significantly affect pH. However, as expected, increasing amounts of Ca had the effect of decreasing the pH (Table 4).

##### 2) Total-P

Three samples of each soil were used in the digestion phase of this experiment. The respective extracts were prepared in triplicate for P determination. Each transmittance (% T) measurement was also done in triplicate. % T averages were calculated down to the sample replicate level and are listed in Table 5. Then, the respective total-P contents were computed and the averages for each soil taken.

##### 3) Soluble P

After 21 days the suspensions were filtered through Whatman filter paper 42. From the solution phases triplicates were prepared for P measurements as follows: 5 ml of the solution phase were mixed with 4 ml

Table 3: pH vs. Time in the Main Experiment

Day	EC pH	Soil	Added P In mg/Kg of soil					Soil	Added P In mg/Kg of soil				
			0	25	50	100	200		0	25	50	100	200
0	EC dS/m	T1	2.35	2.30	2.26	2.30	2.47	A	2.26	2.27	2.24	2.26	2.31
1	pH		7.50	7.55	7.48	7.45	7.41		7.52	7.52	7.48	7.43	7.40
4			7.38	7.35	7.36	7.34	7.30		7.42	7.41	7.37	7.35	7.35
8			7.34	7.33	7.29	7.27	7.26		7.34	7.32	7.30	7.29	7.33
15			7.27	7.31	7.26	7.24	7.21		7.29	7.31	7.26	7.23	7.30
18			7.24	7.25	7.23	7.22	7.20		7.28	7.30	7.25	7.23	7.28
21			7.22	7.23	7.20	7.20	7.18		7.30	7.30	7.26	7.23	7.27
0	EC dS/m	T2	2.30	2.28	2.27	2.29	2.39	B	2.26	2.25	2.25	2.26	2.43
1	pH		7.51	7.48	7.50	7.36	7.36		7.60	7.61	7.59	7.59	7.52
4			7.34	7.38	7.31	7.25	7.27		7.55	7.55	7.55	7.53	7.49
8			7.26	7.24	7.24	7.18	7.20		7.54	7.53	7.54	7.49	7.45
15			7.24	7.19	7.19	7.16	7.15		7.53	7.50	7.48	7.50	7.49
18			7.22	7.17	7.16	7.14	7.13		7.49	7.47	7.48	7.46	7.45
21			7.21	7.16	7.15	7.13	7.12		7.49	7.48	7.50	7.46	7.41
0	EC dS/m	T3	2.34	2.26	2.29	2.27	2.34	C	2.28	2.24	2.24	2.29	2.30
1	pH		7.48	7.45	7.42	7.46	7.44		7.58	7.58	7.59	7.62	7.63
4			7.38	7.40	7.37	7.43	7.41		7.52	7.51	7.53	7.56	7.56
8			7.35	7.36	7.34	7.41	7.38		7.49	7.50	7.55	7.52	7.51
15			7.34	7.37	7.32	7.36	7.33		7.47	7.49	7.54	7.47	7.43
18			7.33	7.34	7.33	7.35	7.29		7.50	7.50	7.50	7.46	7.45
21			7.33	7.33	7.33	7.29	7.29		7.46	7.51	7.49	7.49	7.47
0	EC dS/m	T5	2.32	2.25	2.25	2.25	2.26	D	2.27	2.21	2.22	2.24	2.23
1	pH		7.44	7.42	7.44	7.41	7.36		7.62	7.58	7.55	7.50	7.52
4			7.34	7.33	7.31	7.30	7.25		7.54	7.49	7.50	7.48	7.46
8			7.30	7.29	7.25	7.18	7.18		7.50	7.46	7.44	7.41	7.42
15			7.24	7.22	7.22	7.14	7.11		7.45	7.42	7.40	7.36	7.36
18			7.22	7.24	7.23	7.15	7.12		7.42	7.38	7.38	7.32	7.36
21			7.23	7.18	7.16	7.14	7.08		7.38	7.38	7.36	7.34	7.32
0	EC dS/m	T8	2.29	2.25	2.26	2.34	2.35	W	2.26	2.23	2.26	2.25	2.23
1	pH		7.54	7.54	7.55	7.55	7.50		7.64	7.57	7.49	7.31	7.29
4			7.43	7.41	7.42	7.44	7.42		7.40	7.41	7.38	7.21	7.22
8			7.38	7.39	7.40	7.35	7.32		7.33	7.33	7.29	7.15	7.10
15			7.34	7.30	7.30	7.28	7.27		7.32	7.32	7.22	7.09	7.10
18			7.31	7.29	7.27	7.25	7.22		7.32	7.30	7.19	7.06	7.08
21			7.28	7.26	7.25	7.22	7.17		7.31	7.28	7.15	7.05	7.08

Table 4: pH vs. Time in the Complementary Experiment

Day #	Added P mg/Kg	pH									
		Soil	Added Calcium in mol/L				Soil	Added Calcium in mol/L			
			0	0.003	0.009	0.024		0	0.003	0.009	0.024
1	0	T3	8.14	7.82	7.51	7.33	A	8.10	7.77	7.53	7.32
4			8.07	7.70	7.48	7.31		8.06	7.66	7.54	7.30
8			7.88	7.64	7.38	7.25		7.86	7.47	7.34	7.20
15			7.68	7.47	7.31	7.16		7.56	7.44	7.28	7.14
18			7.68	7.47	7.30	7.14		7.56	7.44	7.27	7.13
21			7.68	7.46	7.29	7.14		7.56	7.44	7.27	7.13
1	100		8.01	7.66	7.47	7.18		8.00	7.74	7.44	7.29
4			7.82	7.63	7.40	7.17		7.96	7.73	7.40	7.24
8			7.64	7.59	7.32	7.17		7.94	7.53	7.31	7.16
15			7.68	7.47	7.32	7.12		7.68	7.38	7.23	7.08
18			7.68	7.47	7.30	7.11		7.66	7.38	7.22	7.08
21			7.68	7.47	7.29	7.11		7.65	7.38	7.22	7.08
1	200	7.86	7.55	7.45	7.09	7.89	7.63	7.44	7.30		
4		7.77	7.42	7.36	7.08	7.78	7.58	7.33	7.15		
8		7.75	7.63	7.28	7.08	7.74	7.50	7.27	7.12		
15		7.67	7.42	7.32	7.04	7.62	7.31	7.18	7.04		
18		7.68	7.41	7.31	7.03	7.61	7.32	7.18	7.02		
21		7.68	7.41	7.29	7.03	7.61	7.32	7.18	7.02		
1	0	T8	8.40	7.85	7.58	7.32	W	7.98	7.69	7.54	7.34
4			8.00	7.75	7.52	7.24		7.81	7.59	7.41	7.24
8			7.90	7.64	7.50	7.22		7.63	7.40	7.36	7.08
15			7.60	7.43	7.23	7.13		7.34	7.33	7.29	7.06
18			7.60	7.34	7.16	7.05		7.32	7.30	7.28	7.04
21			7.49	7.34	7.17	7.04		7.32	7.29	7.28	7.04
1	100		8.20	7.70	7.50	7.29		7.83	7.63	7.37	7.34
4			8.00	7.66	7.46	7.18		7.79	7.59	7.27	7.23
8			7.87	7.61	7.35	7.16		7.69	7.36	7.13	7.10
15			7.58	7.39	7.23	7.03		7.32	7.27	7.08	7.04
18			7.50	7.33	7.21	7.01		7.32	7.27	7.07	7.04
21			7.50	7.33	7.20	7.01		7.31	7.26	7.07	7.04
1	200	8.10	7.66	7.46	7.25	7.66	7.52	7.35	7.31		
4		7.85	7.52	7.33	7.06	7.62	7.46	7.25	7.17		
8		7.81	7.54	7.27	7.08	7.67	7.30	7.09	7.06		
15		7.60	7.32	7.17	7.02	7.32	7.26	7.08	7.04		
18		7.60	7.29	7.15	7.00	7.32	7.25	7.08	7.03		
21		7.49	7.29	7.15	7.00	7.33	7.24	7.08	7.03		

Table 5: Determination of Total P

Soil	%T	Abs.	Flask ppm	In Soil			
				ppm	mole/Kg	average	std. dev.
T1	7	1.155	1.63	510.1	1.6E-02	1.6E-02	4.8E-04
	8	1.097	1.55	484.4	1.6E-02		
	8	1.097	1.55	484.4	1.6E-02		
T2	20	0.699	0.99	308.5	1.0E-02	1.0E-02	3.3E-04
	18	0.745	1.05	328.7	1.1E-02		
	19	0.721	1.02	318.3	1.0E-02		
T3	23	0.638	0.90	281.6	9.1E-03	8.3E-03	7.0E-04
	28	0.553	0.78	243.8	7.9E-03		
	28	0.553	0.78	243.8	7.9E-03		
T5	45	0.347	0.49	152.7	4.9E-03	5.1E-03	2.2E-04
	42	0.377	0.53	166.0	5.4E-03		
	44	0.357	0.50	157.0	5.1E-03		
T8	18	0.745	1.05	328.7	1.1E-02	1.1E-02	2.0E-04
	17	0.770	1.09	339.7	1.1E-02		
	18	0.745	1.05	328.7	1.1E-02		
A	37	0.432	0.61	190.3	6.1E-03	6.1E-03	1.7E-04
	38	0.420	0.59	185.2	6.0E-03		
	36	0.444	0.63	195.6	6.3E-03		
B	54	0.268	0.38	117.7	3.8E-03	3.8E-03	6.7E-05
	53	0.276	0.39	121.3	3.9E-03		
	54	0.268	0.38	117.7	3.8E-03		
C	52	0.284	0.40	125.0	4.0E-03	3.9E-03	1.2E-04
	54	0.268	0.38	117.7	3.8E-03		
	53	0.276	0.39	121.3	3.9E-03		
D	52	0.284	0.40	125.0	4.0E-03	4.0E-03	1.3E-04
	54	0.268	0.38	117.7	3.8E-03		
	52	0.284	0.40	125.0	4.0E-03		
W	58	0.237	0.33	104.0	3.4E-03	3.5E-03	1.7E-04
	55	0.260	0.37	114.2	3.7E-03		
	56	0.252	0.35	110.7	3.6E-03		

of ascorbic acid-molybdate reagent and completed to 25 ml. The averages of %T are listed in Tables 6 and 7, and

- ppm in the flask was computed as described above
- ppm in the solution phase is - (ppm in flask) x 25/5
- Since it is a 1:5 soil solution ratio, the ppm in soil (or mg/kg) - ppm in solution x 5
- In sum: (mg/kg soil) - (ppm flask x 25)

We can observe at this point that:

i) There is fixation of P by the soils which is clearly noticeable when 200 mg/kg of P is added.

ii) The fixation increases with added calcium (Table 7)

4) Soluble Calcium and Magnesium

The atomic absorption spectrophotometer gives the concentrations of the measured solutions in ppm, provided it was previously calibrated. The results are listed in Tables 6 and 7.

Since there is a particular range where the AA calibration curve is linear and where there is less interference, suitable aliquots of the soil extract had to be taken according to the level of Ca added, in order to make up the working solutions, prepared as follows:

Added Ca	Aliquot	SrCl <sub>2</sub> (1000ppm)	Dil.fact.æ
0.000 M	5 mL	10 mL	5
0.003 M	3 mL	10 mL	3
0.010 M	1 mL	10 mL	1
0.025 M (dil.10x)	3 mL	10 mL	0.3

Table 6: Raw Data from Main Experiment

Added P mg/Kg soil	EC dS/m	Phosphorus				x	Calcium		Magnesium	
		%T	Flask Abs.	ppm	Soil mg/Kg		Flask ppm	Solution mole/L	Flask ppm	Solution mole/L
T1	0	2.19	60	0.222	0.31	8	4.78	0.0060	1.22	0.0025
	25	2.20	52	0.284	0.40	10	4.68	0.0059	1.20	0.0025
	50	2.21	41	0.387	0.55	14	4.63	0.0058	1.20	0.0025
	100	2.23	30	0.523	0.74	18	4.53	0.0057	1.24	0.0026
	200	2.25	17	0.770	1.09	27	4.45	0.0056	1.40	0.0029
T2	0	2.22	72	0.143	0.20	5	4.90	0.0061	1.26	0.0026
	25	2.24	61	0.215	0.30	8	4.80	0.0060	1.23	0.0026
	50	2.19	52	0.284	0.40	10	4.70	0.0059	1.17	0.0024
	100	2.21	37	0.432	0.61	15	4.59	0.0057	1.12	0.0023
	200	2.25	20	0.699	0.99	25	4.50	0.0056	1.37	0.0029
T3	0	2.25	88	0.056	0.08	2	4.85	0.0061	1.02	0.0021
	25	2.22	86	0.066	0.09	2	4.82	0.0060	1.05	0.0022
	50	2.24	78	0.108	0.15	4	4.78	0.0060	1.08	0.0023
	100	2.20	66	0.180	0.25	6	4.80	0.0060	1.08	0.0022
	200	2.28	44	0.357	0.50	13	4.55	0.0057	1.19	0.0025
T5	0	2.17	93	0.032	0.04	1	4.88	0.0061	1.19	0.0025
	25	2.19	90	0.046	0.06	2	4.77	0.0060	1.23	0.0026
	50	2.20	87	0.060	0.08	2	4.84	0.0061	1.28	0.0027
	100	2.19	77	0.114	0.16	4	4.80	0.0060	1.28	0.0027
	200	2.20	52	0.284	0.40	10	4.71	0.0059	1.16	0.0024
T8	0	2.22	67	0.174	0.24	6	4.26	0.0053	1.08	0.0022
	25	2.20	64	0.194	0.27	7	4.22	0.0053	1.13	0.0024
	50	2.21	56	0.252	0.35	9	4.19	0.0052	1.09	0.0023
	100	2.22	45	0.347	0.49	12	4.22	0.0053	1.31	0.0027
	200	2.26	18	0.745	1.05	26	4.18	0.0052	1.30	0.0027

Table 6 (cont.): Raw Data from Main Experiment

Added P mg/Kg soil	EC dS/m	Phosphorus				x	Calcium		Magnesium	
		%T	Flask Abs.	ppm	Soil mg/Kg		Flask ppm	Solution mole/L	Flask ppm	Solution mole/L
A	0	2.18	96	0.018	0.02	1	4.30	0.0054	1.80	0.0038
	25	2.18	95	0.022	0.03	1	4.28	0.0054	1.87	0.0039
	50	2.22	91	0.041	0.06	1	4.29	0.0054	1.86	0.0039
	100	2.18	80	0.097	0.14	3	4.31	0.0054	1.85	0.0039
	200	2.18	52	0.264	0.40	10	4.22	0.0053	1.93	0.0040
B	0	2.17	98	0.009	0.01	0	4.13	0.0052	2.10	0.0044
	25	2.19	97	0.013	0.02	0	4.15	0.0052	2.15	0.0045
	50	2.20	96	0.018	0.02	1	4.06	0.0051	2.16	0.0045
	100	2.19	92	0.036	0.05	1	4.03	0.0050	2.20	0.0046
	200	2.20	71	0.149	0.21	5	4.05	0.0051	2.18	0.0045
C	0	2.17	98	0.009	0.01	0	4.33	0.0054	2.10	0.0044
	25	2.18	97	0.013	0.02	0	4.35	0.0054	1.96	0.0041
	50	2.20	96	0.018	0.02	1	4.39	0.0055	1.94	0.0040
	100	2.19	92	0.036	0.05	1	4.38	0.0055	1.88	0.0039
	200	2.20	73	0.137	0.19	5	4.41	0.0055	1.87	0.0039
D	0	2.16	98	0.009	0.01	0	4.53	0.0057	1.82	0.0038
	25	2.17	97	0.013	0.02	0	4.60	0.0058	1.78	0.0037
	50	2.19	95	0.022	0.03	1	4.54	0.0057	1.73	0.0036
	100	2.18	92	0.036	0.05	1	4.63	0.0058	1.68	0.0035
	200	2.20	75	0.125	0.17	4	4.67	0.0058	1.69	0.0035
W	0	2.22	97	0.013	0.02	0	6.62	0.0083	0.38	0.0008
	25	2.20	95	0.022	0.03	1	6.67	0.0083	0.38	0.0008
	50	2.23	91	0.041	0.06	1	6.65	0.0083	0.38	0.0008
	100	2.18	78	0.108	0.15	4	6.68	0.0084	0.38	0.0008
	200	2.17	54	0.268	0.38	9	6.70	0.0084	0.37	0.0008

Table 7: Raw Data from the Complementary Experiment

Soil	Added Ca mole/L	Added P mg/Kg	EC dS/m	Phosphorus				X	Calcium		Magnesium	
				%T	Flask Abs.	ppm	Soil mg/Kg		Flask ppm	Solution mole/L	Flask ppm	Solution mole/L
T3	0.000	0	0.54	69	0.161	0.23	6	5	2.65	0.0007	0.7200	0.0003
		100	0.54	38	0.420	0.59	15		2.23	0.0006	0.6290	0.0003
		200	0.57	17	0.770	1.09	27		2.35	0.0006	0.6610	0.0004
	0.003	0	1.09	79	0.102	0.14	4	3	4.87	0.0020	1.2900	0.0009
		100	1.10	54	0.268	0.38	9		4.61	0.0020	1.2490	0.0009
		200	1.10	25	0.602	0.85	21		4.69	0.0020	1.4000	0.0010
	0.009	0	2.26	89	0.051	0.07	2	1	4.95	0.0062	1.0140	0.0021
		100	2.20	66	0.160	0.25	6		4.65	0.0061	1.0720	0.0022
		200	2.25	45	0.347	0.49	12		4.53	0.0057	1.2070	0.0025
	0.024	0	5.52	93	0.032	0.04	1	0	4.73	0.0197	0.5760	0.0040
		100	5.62	80	0.097	0.14	3		4.74	0.0198	0.5860	0.0041
		200	5.59	52	0.284	0.40	10		4.76	0.0198	0.5910	0.0041
T6	0.000	0	0.48	49	0.310	0.44	11	5	3.59	0.0009	1.2500	0.0005
		100	0.50	25	0.602	0.85	21		4.05	0.0010	1.2800	0.0005
		200	0.49	16	0.796	1.12	28		3.19	0.0008	1.0700	0.0004
	0.003	0	1.02	57	0.244	0.34	9	3	5.20	0.0022	1.9600	0.0014
		100	1.04	36	0.444	0.63	16		5.30	0.0022	1.9000	0.0013
		200	1.04	17	0.770	1.09	27		5.27	0.0022	1.8200	0.0013
	0.009	0	2.19	67	0.174	0.24	6	1	4.26	0.0053	1.0830	0.0023
		100	2.20	46	0.337	0.48	12		4.22	0.0053	1.3140	0.0027
		200	2.24	17	0.770	1.09	27		4.18	0.0052	1.2980	0.0027
	0.024	0	5.60	72	0.143	0.20	5	0	4.62	0.0193	0.6970	0.0048
		100	5.53	49	0.310	0.44	11		4.66	0.0194	0.6740	0.0047
		200	5.64	27	0.569	0.80	20		4.60	0.0192	0.7060	0.0049

Table 7 (cont.): Raw Data from the Complementary Experiment

Soil	Added Ca mole/L	Added P mg/Kg	EC dS/m	Phosphorus				X	Calcium		Magnesium	
				%T	Flask Abs.	ppm	Soil mg/Kg		Flask ppm	Solution mole/L	Flask ppm	Solution mole/L
A	0.000	0	0.47	75	0.125	0.17	4	5	2.65	0.0007	0.7200	0.0003
		100	0.49	70	0.155	0.22	5		4.46	0.0011	1.3700	0.0006
		200	0.48	38	0.420	0.59	15		4.32	0.0011	1.3500	0.0006
	0.003	0	1.02	93	0.032	0.04	1	3	5.19	0.0022	1.9400	0.0013
		100	0.99	73	0.137	0.19	5		5.15	0.0021	1.9600	0.0014
		200	1.11	39	0.409	0.58	14		5.09	0.0021	1.9600	0.0014
	0.009	0	2.17	96	0.018	0.02	1	1	4.35	0.0054	1.8300	0.0038
		100	2.23	79	0.102	0.14	4		4.32	0.0054	1.8700	0.0039
		200	2.19	52	0.284	0.40	10		4.21	0.0053	1.9100	0.0040
	0.024	0	5.47	97	0.013	0.02	0	0	4.07	0.0170	0.9680	0.0069
		100	5.41	85	0.071	0.10	2		4.05	0.0169	0.9230	0.0064
		200	5.49	58	0.237	0.33	8		4.00	0.0167	0.9220	0.0064
W	0.000	0	0.44	93	0.032	0.04	1	5	5.91	0.0015	0.5590	0.0002
		100	0.42	66	0.180	0.25	6		6.36	0.0016	0.4160	0.0002
		200	0.41	33	0.481	0.68	17		5.14	0.0013	0.4270	0.0002
	0.003	0	0.88	94	0.027	0.04	1	3	6.50	0.0027	0.5190	0.0004
		100	0.89	70	0.155	0.22	5		6.48	0.0027	0.4940	0.0003
		200	0.89	46	0.337	0.48	12		6.42	0.0027	0.5270	0.0004
	0.009	0	2.20	97	0.013	0.02	0	1	6.69	0.0084	0.3820	0.0008
		100	2.17	79	0.102	0.14	4		6.66	0.0083	0.3700	0.0008
		200	2.15	55	0.260	0.37	9		6.73	0.0084	0.3710	0.0008
	0.024	0	5.48	97	0.013	0.02	0	0	5.04	0.0210	0.3200	0.0022
		100	5.35	80	0.097	0.14	3		5.10	0.0213	0.2900	0.0020
		200	5.45	63	0.201	0.28	7		5.21	0.0217	0.2980	0.0021

Therefore the amount is given by (ppm in extract) - (ppm in flask) x 50/æ = (mg/L of extract) and in mols/L will be:

(mols/L) = (mg/L)/(40E<sup>3</sup> mg/mol) in the case of Ca (A.Wt. = 40).

(mols/L) = (mg/L)/(24E<sup>3</sup> mg/mol) in the case of Mg (A.Wt. = 24)

The results are listed in Tables 6 and 7.

Values of [Ca] close to the ones added were expected. However the measurements gave results a little bit low. Measurements were repeated with new standards but the second set of results confirmed the first. The concentrations of the extracting solutions were then measured and only slight corrections were needed: the 0.010M Ca solution was a 0.009M and the 0.025M was a 0.024M.

The following observations and statements lead to the conclusion that the results were probably correct:

- i) When Ca is added , Mg increases in the solution.
- ii) This increase is of the same order of magnitude than the decrease of [Ca] relatively to the added [Ca].
- iii) The conductivity being as expected, (as shown next) indicates an exchange rather than precipitation mechanism.
- iv) Lindsay and Moreno (1960) consider that the "exchange complex acts as a buffer with regard to changes in the concentration of Ca<sup>++</sup> and Mg<sup>++</sup> in the soil solution" and that "it is reasonable to assume that the concentrations of these cations are controlled by the exchange complex".

v) Mehadi & Taylor (1968) assume a 0.005M Ca concentration for a 0.01M  $\text{CaCl}_2$  solution: "the  $C_o$  term ... was computed ... assuming a pCa of 2.3 and ... the use of the Debye-Huckel equation for estimating the activity of ionic species in an ionic strength of 0.01M  $\text{CaCl}_2$ ."

#### 5) Conductivity and Ionic Strength

The conductivity of the suspensions did not change significantly from the day zero (Table 3) to the last day (Table 6). Conductivities of the solution phase after filtration are listed in Tables 6 and 7. These conductivities were measured as means of assessing the ionic strength of the solutions, specially when none or low amounts of electrolyte were added to the soils. This I.S. calculation is possible by the use of the empirical linear regression  $I=0.013EC$  established by Griffin and Jurinak (1973<sub>a</sub>). The ionic strength is needed for estimation of activity coefficients of ions in the solutions. The values of ionic strength computed by the previous equation (Table 8) confirm the direct calculation of the two more concentrated solutions by equation  $I = 3C$  established for  $\text{CaCl}_2$ .

A solution of 0.025M gave a AA reading of 5.73 ppm; dilution factor =  $50/0.3$  results in 955.0 ppm which (+ 40) represents 0.024M;  $0.024M \times 3 = 0.072 = \text{Ionic Strength}$ .

Solution 0.010M gave a AA reading of 7.35 ppm; dilution factor =  $50/1$  results in 367.5 ppm which (+ 40) represents 0.0092M;  $0.0092M \times 3 = 0.028 = \text{Ionic Strength}$ .

## Precision and Accuracy

### a) General Considerations

Precision describes the reproducibility of results i.e. the agreement between two or more measurements made in the same way. A way of expressing precision is through the calculation of the standard deviation. A better precision is obtained when the number of replicates is high.

Accuracy refers to how close a measurement is to the true value. Accuracy can never be unambiguously evaluated because it requires the knowledge of the true value of what is being sought by the analytical determination. Therefore, at best, a researcher can only estimate the accuracy of data.

Due to the large uncertainty carried by the solubility constants used in the computation of SAC and to values raised to high powers, attempts to improve the precision of measurements are not as important as the search for accuracy.

The pH, conductivity, P, Ca and Mg were all measured by electronic instruments. These instruments deliver a level of precision higher than the uncertainty borne by the soil sampling itself. Also these electronic instruments are susceptible to systematic errors which cannot be detected by replication.

### b) Strategy Used

The complementary experiment, whose main goal was to provide data for the study of the influence of added Ca on SAC, was designed in such a way that pertinent suspensions of the main experiment were replicated:

● choice of soils: two from Tarrafal, one from Justino Lopes and the American soil. The two from Tarrafal were among the ones with very similar data.

● choice of added P levels: zero, 100 and 200 mg/kg soil. The values for 25 and 50 would be interpolated if necessary.

The determination of the total-P required a more classical procedures (triplicate samples) owing to a more random type of error carried by the digestion part of the experiment. The amount of coarse sand in a 2g sample of a soil may differ from another 2g taken from the same soil, and affects the results of the acid attack.

#### c) Presentation of the Data

All the pertinent determinations for SAC calculations, along with the appropriate units, are compiled in Table 8. The conductivity is the average of 8 measurements, (5 in the main experiment and 3 in the complementary) since there was no significant difference among them, when P was added.

All other values are the averages (when applicable) of the ones in the two experiments (Tables 6 and 7).

Soluble P is expressed in mol/L, as follows:

$$(\text{mg/kg soil})/5 = \text{mg/L of solution}$$

$$(\text{mg/L of solution})/(30973 \text{ mg/mol}) = \text{mol/L}$$

Table 8: Analytical Data after Treatment

Soil	Total P mole/Kg	Added Ca mole/L	EC dS/m	Ionic St. calculated from EC	Added P mg/Kg	pH	Soluble P mol/L	Soluble Ca mol/L	Soluble Mg mol/L
T1	2E-02	0.009	2.22	0.029	0	7.22	6.0E-05	6.0E-03	2.5E-03
					25	7.23	6.6E-05	6.9E-03	2.6E-03
					50	7.20	8.8E-05	5.8E-03	2.5E-03
					100	7.20	1.2E-04	5.7E-03	2.6E-03
					200	7.18	1.8E-04	5.6E-03	2.9E-03
T2	1E-02	0.009	2.22	0.029	0	7.21	3.2E-05	6.1E-03	2.6E-03
					25	7.16	4.9E-05	6.0E-03	2.6E-03
					50	7.15	6.5E-05	5.9E-03	2.4E-03
					100	7.13	9.8E-05	5.7E-03	2.3E-03
					200	7.12	1.6E-04	5.6E-03	2.9E-03
T3	6E-03	0.000	0.55	0.007	0	7.68	3.6E-05	6.6E-04	3.0E-04
					100	7.68	9.8E-05	5.6E-04	2.6E-04
					200	7.68	1.8E-04	5.9E-04	3.6E-04
		0.003	1.10	0.014	0	7.46	2.3E-05	2.0E-03	9.0E-04
					100	7.47	6.1E-05	2.0E-03	6.7E-04
					200	7.41	1.4E-04	2.0E-03	9.7E-04
	0.009	2.24	0.029	0	7.31	1.2E-05	6.1E-03	2.1E-03	
				25	7.33	1.5E-05	6.0E-03	2.3E-03	
				50	7.33	2.4E-05	6.0E-03	2.2E-03	
	0.024	5.58	0.072	0	7.29	4.1E-05	6.0E-03	2.2E-03	
				100	7.29	8.0E-05	5.7E-03	2.5E-03	
				200	7.29	8.0E-05	5.7E-03	2.5E-03	
T5	5E-03	0.009	2.19	0.028	0	7.23	6.9E-06	6.1E-03	2.6E-03
					25	7.18	1.0E-05	6.0E-03	2.6E-03
					50	7.16	1.3E-05	6.1E-03	2.7E-03
					100	7.14	2.6E-05	6.0E-03	2.7E-03
					200	7.08	6.5E-05	5.9E-03	2.4E-03
T8	1E-02	0.000	0.49	0.006	0	7.49	7.0E-05	9.0E-04	5.2E-04
					100	7.50	1.4E-04	1.0E-03	5.3E-04
					200	7.49	1.8E-04	8.0E-04	4.5E-04
		0.003	1.03	0.013	0	7.34	5.5E-05	2.2E-03	1.4E-03
					100	7.33	1.0E-04	2.2E-03	1.3E-03
					200	7.29	1.8E-04	2.2E-03	1.3E-03
	0.009	2.22	0.029	0	7.23	3.9E-05	5.3E-03	2.3E-03	
				25	7.26	4.4E-05	5.3E-03	2.4E-03	
				50	7.25	5.7E-05	5.2E-03	2.3E-03	
	0.024	5.59	0.073	0	7.21	7.8E-05	5.3E-03	2.7E-03	
				100	7.21	7.8E-05	5.3E-03	2.7E-03	
				200	7.16	1.7E-04	5.2E-03	2.7E-03	
0.024	5.59	0.073	0	7.04	3.2E-05	1.9E-02	4.8E-03		
			100	7.01	7.0E-05	1.9E-02	4.7E-03		
			200	7.00	1.3E-04	1.9E-02	4.9E-03		

Table 8 (cont): Analytical Data after Treatment

Soil	Total P mols/Kg	Added Ca mols/L	EC dS/m	Ionic St. calculated from EC	Added P mg/Kg	pH	Soluble P mol/L	Soluble Ca mol/L	Soluble Mg mol/L	
A	6E-03	0.000	0.48	0.006	0	7.56	2.8E-05	6.6E-04	3.0E-04	
					100	7.55	3.5E-05	1.1E-03	8.7E-04	
					200	7.51	9.6E-05	1.1E-03	5.6E-04	
		0.003	1.04	0.013	0	7.44	6.9E-06	2.2E-03	1.3E-03	
					100	7.38	3.1E-05	2.1E-03	1.4E-03	
					200	7.32	9.3E-05	2.1E-03	1.4E-03	
	0.009	2.19	0.028	0	7.28	3.7E-06	5.4E-03	3.8E-03		
				25	7.30	4.8E-06	5.4E-03	3.9E-03		
				50	7.25	9.0E-06	5.4E-03	3.9E-03		
	100	7.23	2.2E-05	5.4E-03	3.9E-03	100	7.23	2.2E-05	5.4E-03	3.9E-03
						200	7.23	6.5E-05	5.3E-03	4.0E-03
						0	7.13	2.7E-06	1.7E-02	6.9E-03
0.024	5.46	0.071	100	7.08	1.6E-05	1.7E-02	6.4E-03			
			200	7.02	5.4E-05	1.7E-02	6.4E-03			
			0	7.49	1.7E-06	5.2E-03	4.4E-03			
B	4E-03	0.009	2.19	0.028	25	7.48	2.7E-06	5.2E-03	4.5E-03	
					50	7.50	3.7E-06	5.1E-03	4.5E-03	
					100	7.46	7.9E-06	5.0E-03	4.6E-03	
					200	7.41	3.4E-05	5.1E-03	4.5E-03	
					0	7.46	1.7E-06	5.4E-03	4.4E-03	
C	4E-03	0.009	2.19	0.028	25	7.51	2.7E-06	5.4E-03	4.1E-03	
					50	7.49	3.7E-06	5.4E-03	4.0E-03	
					100	7.49	7.9E-06	5.5E-03	3.9E-03	
					200	7.47	3.1E-05	5.5E-03	3.9E-03	
					0	7.38	1.7E-06	5.7E-03	3.8E-03	
D	4E-03	0.009	2.18	0.028	25	7.38	2.7E-06	5.8E-03	3.7E-03	
					50	7.36	4.8E-06	5.7E-03	3.6E-03	
					100	7.34	7.9E-06	5.8E-03	3.5E-03	
					200	7.32	2.8E-05	5.8E-03	3.5E-03	
					0	7.32	6.9E-06	1.5E-03	2.3E-04	
W	4E-03	0.000	0.42	0.006	100	7.31	4.1E-05	1.8E-03	1.7E-04	
					200	7.33	1.1E-04	1.3E-03	1.8E-04	
					0	7.29	5.8E-06	2.7E-03	3.6E-04	
		0.003	0.89	0.012	100	7.26	3.5E-05	2.7E-03	3.4E-04	
					200	7.24	7.7E-05	2.7E-03	3.7E-04	
					0	7.30	2.7E-06	8.3E-03	8.0E-04	
	0.009	2.19	0.028	25	7.28	4.8E-06	8.3E-03	7.9E-04		
				50	7.15	9.0E-06	8.3E-03	7.9E-04		
				100	7.06	2.4E-05	8.3E-03	7.8E-04		
	200	7.08	6.0E-05	8.4E-03	7.8E-04	200	7.08	6.0E-05	8.4E-03	7.8E-04
						0	7.04	2.7E-06	2.1E-02	2.2E-03
						100	7.04	2.2E-05	2.1E-02	2.0E-03
0.024	5.43	0.071	200	7.03	4.6E-05	2.2E-02	2.1E-03			

### Computation of Solid Activity Coefficients

#### Salt Solid Activity Coefficients

##### a) Computation of Ionic Species Activities

For the calculation of solid activity coefficients the ionic activity product has to be known. The ionic activity product is the activity of the ionic species in solution.

Therefore the aqueous activity of the concerned ions must be calculated first.

Those ions are:  $(Ca^{++})$ ,  $(Mg^{++})$ ,  $(H^+)$ ,  $(OH^-)$ ,  $(H_2PO_4^-)$  and  $(HPO_4^-)$ .  $(PO_4^{3-})$  was not calculated because the IAP of the selected minerals can be expressed in terms of  $(HPO_4^-)$  or  $(H_2PO_4^-)$  once the phosphate ion activities are interrelated and because at the observed pHs,  $HPO_4^-$  and  $H_2PO_4^-$  are the predominant species.

In order to calculate those activities from the measured concentrations, the estimation of the ionic activity coefficients is necessary. Generally the Debye-Huckel extended equation is used and respective tables are provided in the literature. However, for practical reasons the Davies equation has been often used; its single variable is "more readily adapted for computer use" (Lindsay 1979). Indeed, the ionic strength observed in the experiments were: 0.006, 0.013, 0.028, 0.072 which are intermediate values, not found in tables.

In order to improve accuracy, the activity coefficients were taken from a computer generated Table (prepared by the author) rather than by interpolation or approximation of values from tables found in the

literature. The thermodynamic constants used were taken from Lindsay (1979).

For phosphates it is generally assumed that only orthophosphoric acid species contribute significantly to the total phosphorus in solution (Lindsay 1979). Therefore the total P concentration in solution [total P] can be expressed in terms of activities as follows:

$$[Total P] = \frac{(H_3PO_4^o)}{\gamma_{H_3PO_4^o}} + \frac{(H_2PO_4^-)}{\gamma_{H_2PO_4^-}} + \frac{(HPO_4^{2-})}{\gamma_{HPO_4^{2-}}} + \frac{(PO_4^{3-})}{\gamma_{PO_4^{3-}}} \quad (5)$$

Using the appropriate equilibrium constants,  $(H^+)$ , and the following equations:

$$(H_3PO_4^o) = (H^+) (H_2PO_4^-) \bullet 10^{2.15} \quad (6)$$

$$(H_2PO_4^-) = (H^+) (HPO_4^{2-}) \bullet 10^{7.20} \quad (7)$$

$$(HPO_4^{2-}) = (H^+) (PO_4^{3-}) \bullet 10^{12.35} \quad (8)$$

$$(PO_4^{3-}) = (H_2PO_4^-)/(H^+)^2 \bullet 10^{-19.55} \quad (9)$$

We can express each term on the right side of equation (5) in terms of  $H_2PO_4^-$  and get (Lindsay 1979, eq. 12.8):

$$(H_2PO_4^-) = \frac{[Total P]}{10^{2.15} (H^+) + \frac{1}{\gamma_{H_2PO_4^-}} + \frac{10^{-7.20}}{\gamma_{HPO_4^{2-}} (H^+)} + \frac{10^{-19.55}}{\gamma_{PO_4^{3-}} (H^+)^2}} \quad (10)$$

or express in terms of  $(\text{HPO}_4^{2-})$  as:

$$(\text{H}_3\text{PO}_4^{\circ}) = (\text{H}^+)^2 (\text{HPO}_4^{2-}) \bullet 10^{9.35} \quad (7) \text{ in } (6)$$

$$(\text{H}_2\text{PO}_4^-) = (\text{H}^+) (\text{HPO}_4^{2-}) \bullet 10^{7.20} \quad \text{equation } (7)$$

$$(\text{PO}_4^{3-}) = (\text{HPO}_4^{2-})/(\text{H}^+) \bullet 10^{-12.35} \quad (7) \text{ in } (9)$$

and get:

$$(\text{HPO}_4^{2-}) = \frac{[\text{Total P}]}{10^{9.35} (\text{H}^+)^2 + \frac{10^{7.20} (\text{H}^+)}{\gamma_{\text{H}_2\text{PO}_4^-}} + \frac{1}{\gamma_{\text{HPO}_4^{2-}}} + \frac{10^{-12.35}}{(\text{H}^+)}} \quad (11)$$

The calculation of  $(\text{Ca}^{2+})$  is based on the following expression:

$$[\text{Total P}] = \frac{(\text{H}_3\text{PO}_4^{\circ})}{\gamma_{\text{H}_3\text{PO}_4^{\circ}}} + \frac{(\text{H}_2\text{PO}_4^-)}{\gamma_{\text{H}_2\text{PO}_4^-}} + \frac{(\text{HPO}_4^{2-})}{\gamma_{\text{HPO}_4^{2-}}} + \frac{(\text{PO}_4^{3-})}{\gamma_{\text{PO}_4^{3-}}} \quad (12)$$

After similar modification  $(\text{Ca})$  can be expressed in terms of  $[\text{total Ca}]$ ,  $(\text{PO}_4^{3-})$ ,  $(\text{H}^+)$  and equilibrium constants.

The application of the resulting equation of the experimental data showed no significant modification of the results obtained if only the first term of equation (12) was retained. This is due to  $(\text{PO}_4^{3-})$  activity being very low in the range of pH of the soils. Therefore the following expression was used.

$$(\text{Ca}^{2+}) = \gamma_{\text{Ca}^{2+}} \times [\text{total Ca}]$$

The same reasoning was applied to Mg resulting in:

$$(\text{Mg}^{2+}) = \gamma_{\text{Mg}^{2+}} \times [\text{total Mg}]$$

The results of these computations are listed in Tables 9 and 10.

### b) Computation of Ionic Activity Products

The most common calcium phosphates cited in the literature as present in alkaline soils are: Dicalcium Phosphate Dihydrate (or Brushite), Dicalcium Phosphate (or Monetite), Octocalcium Phosphate and Hydroxyapatite. The last three were chosen for the SAC calculations.

Bobierite, a magnesium phosphate, was also chosen; Bobierite is, as well as Newberryite, reported among the least soluble of the very soluble magnesium phosphates (Lindsay 1979).

The following reactions (taken from Lindsay 1979) were considered:

	log Ksp
(DCP) $\text{CaHPO}_4 + \text{H}^+ = \text{Ca}^{2+} + \text{H}_2\text{PO}_4^-$	0.30
(OCP) $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O} + 5\text{H}^+ = 4\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + 2.5\text{H}_2\text{O}$	11.76
(HA) $\text{Ca}_5(\text{PO}_4)_3 \text{OH} + 7\text{H}^+ = 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	14.46
(Bob) $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} + 4\text{H}^+ = 3\text{Mg}^{2+} + 2\text{H}_2\text{PO}_4^- + 8\text{H}_2\text{O}$	14.10

Since the pH range of the soils favors  $\text{HPO}_4^{2-}$  the IAP expressions were computed in terms of  $\text{HPO}_4^{2-}$  by substituting  $-\log [\text{Eq. (7)}] = \text{pH}_2\text{PO}_4 \approx \text{pH} + \text{pHPO}_4 - 7.20$  for  $\text{pH}_2\text{PO}_4$  in the following equations:

Dicalcium Phosphate	$\text{pDCP} = \text{pCa} - \text{pH} + \text{pH}_2\text{PO}_4 + 0.30$
→	$\text{pDCP} = \text{pCa} + \text{pHPO}_4 - 6.90$
Octocalcium Phosphate	$\text{pOCP} = -5\text{pH} + 4\text{pCa} + 3 \text{pH}_2\text{PO}_4 + 11.76$
→	$\text{pOCP} = -2\text{pH} + 4\text{pCa} + 3\text{pHPO}_4 - 9.84$
Hydroxyapatite	$\text{pHA} = 5\text{pCa} - 7\text{pH} + 3\text{pH}_2\text{PO}_4 + 14.46$
→	$\text{pHA} = 5\text{pCa} - 4\text{pH} + 3\text{pHPO}_4 - 7.14$
Bobierite	$\text{pBob} = 3\text{pMg} - 4\text{pH} + 2\text{H}_2\text{PO}_4 + 14.10$
→	$\text{pBob} = 3\text{pMg} - 2\text{pH} + 2\text{pHPO}_4 - 0.30$

In sum:	p(IAP)	log Ksp
DCP	pCa + pHPO <sub>4</sub>	-6.90
OCP	4pCa + 3pHPO <sub>4</sub> - 2pH	- 9.84
HA	5pCa + 3pHPO <sub>4</sub> - 4pH	- 7.14
Bob	3pMg + 2pHPO <sub>4</sub> - 2pH	- 0.30

### c) Computation of SAC

Considering eq. (2) under the form :

$$g = \frac{IAP}{K_{sp} \times X}$$

the solid activity coefficient  $g$  can be calculated easily from the referred formulations. However the term  $X$  has to be calculated. According to calculations made by Bohn (1982), soils contain 30 moles of substances per kg. Therefore the mole fraction  $X$  of phosphorus in soils is the total P in the soil (expressed in mols/kg) divided by 30.

### Solid Ion Activity Coefficients

Bohn and Bohn (1987) consider single-ion activities as being more convenient. Single ion activities in solids are calculated by similar conventions as in aqueous solutions: 1) The activity of the salt may be expressed as the product of its components' activities. 2) The activity of  $O^{2-}$  is defined as unity (in analogy to the activity of water in aqueous solutions), because its concentration in minerals is far greater than the other ions (except  $OH^-$ ).  $OH^-$  in solids is not an independent entity, acting as if  $H^+$  was neutralizing  $O^{2-}$ . (Bohn, 1990).

Table 9 : Computation of Solid Activity Coefficients at 0.028 I.S.

		a1 = .653		a2 = .531		a3 = .240		Hydroxyapatite 5pCa+4pH+3pHPO4 pKsp = 7.14			Octocalcium P 4pCa+2pH+3pHPO4 pKsp = 9.84			Dicalcium Ph. pCa+pHPO4 pKsp = 6.90			Biolerrite 3pMg+2pH+2pHPO4 pKsp = .30			
Added	Soil	pH	(Ca++)	(Mg++)	Total P	(HPO4)	E+	PIAP	SAC	g+	PIAP	SAC	g+	PIAP	SAC	g+	PIAP	SAC	g+	
P			E-3	E-3	E-3	E-4														
0	T1	7.22	3.2	1.3	15.9	16.8	-2.13	3.6E+12	25	9.81	2013	3	7.34	980	9	3.85	0.83	1		
	T2	7.21	3.3	1.4	10.3	10.7	-1.65	1.4E+12	22	10.38	943	2	7.53	986	9	4.02	0.68	1		
	T3	7.31	3.3	1.1	8.3	4.2	-0.75	2.8E+11	19	11.39	103	2	7.83	338	7	4.91	0.08	1		
	T5	7.23	3.2	1.3	5.1	2.3	0.37	3.5E+10	15	12.34	19	1	8.29	297	7	5.38	0.05	1		
	T8	7.23	2.8	1.2	10.7	13.2	-1.59	1.0E+12	23	10.32	838	2	7.59	707	9	4.01	0.65	1		
	A	7.28	2.9	2.0	6.1	1.3	1.20	4.3E+08	12	13.21	2	1	8.50	123	5	5.25	0.06	1		
	B	7.49	2.7	2.3	3.8	0.7	1.29	5.6E+08	12	13.71	1	1	8.80	98	5	5.19	0.10	1		
	C	7.40	2.9	2.3	3.9	0.7	1.33	5.0E+08	12	13.71	1	1	8.79	98	5	5.27	0.08	1		
	D	7.38	3.0	2.0	4.0	0.6	1.62	2.6E+09	11	13.99	1	1	8.79	98	5	5.06	0.03	1		
	W	7.30	4.4	0.4	3.5	1.0	0.68	3.0E+10	15	12.82	0	1	8.44	243	6	7.50	6.4E-04	0		
25	T1	7.23	3.1	1.3	15.9	21.7	-2.48	7.5E+12	27	9.49	4187	3	7.34	981	10	3.43	1.39	1		
	T2	7.16	3.2	1.4	10.3	16.4	-1.79	2.6E+12	24	10.04	1852	3	7.38	989	10	3.83	0.85	1		
	T3	7.33	3.2	1.2	8.3	5.3	-1.08	8.2E+11	20	11.07	212	2	7.84	418	7	4.59	0.19	1		
	T5	7.18	3.2	1.4	5.1	3.3	0.17	5.6E+10	16	12.03	38	2	8.06	410	7	5.15	0.08	1		
	T8	7.28	2.8	1.2	10.7	15.1	-1.80	3.0E+12	24	10.08	1803	3	7.44	984	9	3.78	0.97	1		
	A	7.30	2.8	2.1	6.1	1.7	0.78	1.1E+10	13	12.83	5	1	8.39	159	5	4.93	0.12	1		
	B	7.48	2.9	2.4	3.8	1.1	0.71	2.1E+10	14	13.11	4	1	8.60	158	5	4.78	0.26	1		
	C	7.51	2.9	2.2	3.9	1.1	0.47	3.8E+10	15	12.95	8	1	8.57	165	5	4.82	0.23	1		
	D	7.38	3.1	2.0	4.0	1.0	0.97	1.1E+10	13	13.21	3	1	8.58	159	5	5.27	0.08	1		
	W	7.28	4.4	0.4	3.5	1.7	-0.09	1.4E+11	17	12.12	44	2	8.20	494	6	7.05	1.5E-03	0		
50	T1	7.20	3.1	1.3	15.9	28.8	-2.69	1.3E+13	29	9.20	8224	3	7.12	1133	10	3.25	2.13	1		
	T2	7.16	3.1	1.3	10.3	20.2	-2.05	4.6E+12	26	9.74	3678	3	7.27	1248	11	3.69	1.19	1		
	T3	7.33	3.2	1.2	8.3	6.8	-1.74	2.7E+12	24	10.43	941	2	7.82	689	9	4.15	0.62	1		
	T5	7.16	3.2	1.4	5.1	4.3	-0.13	1.1E+11	17	11.70	82	2	7.93	544	8	4.90	0.15	1		
	T8	7.25	2.8	1.2	10.7	18.5	-2.16	5.9E+12	26	9.78	3200	3	7.33	1030	10	3.61	1.38	1		
	A	7.25	2.8	2.1	6.1	3.1	0.19	4.3E+10	15	12.15	24	1	8.13	291	7	4.51	0.30	1		
	B	7.50	2.7	2.4	3.8	1.5	0.34	8.2E+10	16	12.07	11	1	8.48	215	6	4.44	0.57	1		
	C	7.49	2.9	2.1	3.9	1.5	0.12	8.0E+10	16	12.56	14	1	8.43	227	6	4.61	0.38	1		
	D	7.36	3.0	1.9	4.0	1.8	0.35	4.7E+10	15	12.55	15	1	8.34	274	6	4.87	0.21	1		
	W	7.15	4.4	0.4	3.5	2.8	-0.25	2.1E+11	18	11.70	117	2	7.97	718	9	6.87	2.3E-03	0		
100	T1	7.20	3.0	1.4	15.9	39.0	-3.03	2.8E+13	31	8.85	18910	3	7.00	1498	11	2.94	4.34	1		
	T2	7.13	3.0	1.2	10.3	30.2	-2.45	1.1E+13	28	9.30	10177	3	7.11	1817	12	3.43	2.17	1		
	T3	7.29	3.2	1.2	8.3	14.4	-2.23	8.0E+12	27	9.85	2628	3	7.40	1135	10	3.81	1.13	1		
	T5	7.14	3.2	1.4	5.1	7.9	-0.84	5.0E+11	20	10.84	488	2	7.87	1004	10	4.40	0.48	1		
	T8	7.21	2.8	1.5	10.7	25.7	-2.37	9.2E+12	28	9.40	8228	3	7.21	1364	11	3.21	3.47	1		
	A	7.23	2.9	2.1	6.1	7.5	-0.88	5.1E+11	20	11.03	318	2	7.74	711	9	3.79	1.58	1		
	B	7.46	2.7	2.4	3.8	3.1	-0.54	3.7E+11	19	11.81	84	2	8.14	448	8	3.88	2.17	1		
	C	7.49	2.9	2.1	3.9	3.2	-0.86	7.7E+11	21	11.58	139	2	8.10	483	8	3.98	1.58	1		
	D	7.34	3.1	1.9	4.0	2.9	-0.28	1.9E+11	18	11.91	85	2	8.12	480	8	4.52	0.48	1		
	W	7.08	4.4	0.4	3.5	6.8	-1.03	1.3E+12	22	10.74	1060	2	7.59	1722	12	6.31	8.4E-03	0		
200	T1	7.18	3.0	1.8	15.9	56.4	-3.39	6.5E+13	34	8.44	47873	4	6.85	2130	13	2.49	12.05	2		
	T2	7.12	3.0	1.5	10.3	48.4	-2.88	3.8E+13	32	8.74	37122	4	6.81	2960	14	2.78	9.88	2		
	T3	7.29	3.0	1.3	8.3	28.2	-2.98	4.7E+13	33	9.08	20701	3	7.14	2089	13	3.08	6.00	1		
	T5	7.08	3.1	1.3	5.1	18.8	-1.89	4.0E+12	25	9.97	4382	3	7.30	2339	13	3.90	1.48	1		
	T8	7.18	2.8	1.4	10.7	64.5	-3.13	5.3E+13	33	8.53	45431	4	6.89	2896	14	2.67	11.98	2		
	A	7.23	2.8	2.1	6.1	21.7	-2.23	1.1E+13	28	9.88	7134	3	7.29	2008	13	2.82	14.84	2		
	B	7.41	2.7	2.4	3.8	12.9	-2.19	1.7E+13	29	10.06	4713	3	7.53	1840	12	2.74	28.27	2		
	C	7.47	2.9	2.1	3.9	12.3	-2.55	3.8E+13	32	9.88	7300	3	7.51	1899	12	2.86	20.90	2		
	D	7.32	3.1	1.9	4.0	10.2	-1.83	7.1E+12	27	10.30	2615	3	7.57	1622	12	3.46	5.24	1		
	W	7.08	4.5	0.4	3.5	17.5	-2.36	2.7E+13	31	8.45	29821	3	7.18	4475	16	5.44	6.1E-02	1		

Table 10: Computation of Solid Activity Coefficients with Added Ca

Soil (totP) E-S	Ca Add.	P Added	pH	Ca E-S	Mg E-S	s1 s2 s3	HPO4 E-S	Hydroxyapatite 5pCa-4pH+3pHPO4 pKsp = 7.14			Octocalcium Ph. 4pCa-2pH+3pHPO4 pKsp = 8.84			Dicalcium Ph. pCa+pHPO4 pKsp = 8.90			Boblerite 3pMg-2pH+2pHPO4 pKsp = 0.30			
								pIAP	SAC	g+	pIAP	SAC	g+	pIAP	SAC	g+	pIAP	SAC	g+	
mol/Kg	M	mg/Kg		mol/L		mol/L														
T3 (8.3)	0	0	7.66	0.5	0.2	.921	2.1	-0.1	6E+10	18	11.94	29	2	8.04	263	6	6.0	8.9	2	
		100	7.66	0.4	0.2	.719	7.2	-1.3	1E+12	22	10.62	800	2	7.69	786	9	4.1	21	2	
		200	7.66	0.4	0.3	.477	10.0	-1.9	4E+12	26	10.10	2002	3	7.41	1123	10	3.4	73	2	
	.003	0	7.48	1.3	0.9	.891	1.0	-0.5	2E+11	17	11.54	72	2	7.92	343	7	4.7	24	2	
		100	7.47	1.3	0.8	.630	2.8	-1.9	3E+12	24	10.27	1334	2	7.51	800	10	3.9	61	2	
		200	7.41	1.3	0.8	.383	6.0	-2.6	2E+13	30	9.28	11017	3	7.18	1983	13	3.2	136	3	
	.024	0	7.14	8.1	1.8	.800	0.2	-0.9	4E+11	20	11.26	142	2	7.94	331	7	5.5	14	2	
		100	7.11	8.1	1.7	.410	0.8	-2.3	1.0E+13	29	8.63	3693	3	7.45	1024	10	4.8	40	2	
		200	7.03	0.0	0.0	.136	1.6	-3.3	1E+14	36	8.97	63712	4	7.01	2621	14	3.8	72	2	
	T8 (10.7)	0	0	7.49	0.6	0.4	.921	3.6	-0.7	2E+11	18	11.07	166	2	7.87	478	8	4.1	30	2
			100	7.60	0.7	0.4	.719	7.1	-1.9	3E+12	24	9.96	2106	3	7.32	1067	10	3.6	67	2
			200	7.49	0.6	0.3	.477	8.7	-1.9	2E+12	23	10.13	1438	2	7.34	1023	10	3.6	46	2
.003		0	7.34	1.4	0.9	.891	2.3	-1.2	6E+11	20	10.84	445	2	7.85	624	9	3.7	98	3	
		100	7.33	1.4	0.8	.630	4.2	-1.9	3E+12	26	9.80	2710	3	7.29	1151	10	3.3	153	3	
		200	7.29	1.4	0.8	.383	6.2	-2.3	7E+12	27	8.43	7144	3	7.12	1993	12	3.1	160	3	
.024		0	7.04	7.9	2.0	.900	0.9	-2.4	9E+12	29	9.59	4955	3	7.32	1067	10	4.2	63	2	
		100	7.01	8.0	1.9	.410	1.6	-3.3	7E+13	36	8.66	42483	4	6.99	2279	13	3.6	102	3	
		200	7.00	0.0	0.0	.136	2.9	-4.0	4E+14	41	7.82	232438	5	6.73	4098	16	3.1	202	3	
A (6.1)		0	0	7.66	0.5	0.2	.921	1.8	0.6	1E+10	13	12.69	9	1	8.18	269	6	5.5	3.5	1
			100	7.65	0.9	0.4	.719	1.9	-0.6	3E+11	18	11.43	126	2	7.96	536	9	4.5	28	2
			200	7.61	0.9	0.4	.477	3.8	-1.3	1E+12	22	10.62	915	2	7.66	1077	10	3.9	46	2
	.003	0	7.44	1.4	0.9	.891	0.3	1.1	6E+09	12	13.07	3	1	8.43	146	6	5.3	22	2	
		100	7.38	1.4	0.9	.630	1.3	-0.6	3E+11	19	11.30	170	2	7.80	620	9	4.1	70	2	
		200	7.32	1.3	0.9	.383	3.8	-1.7	3E+12	26	10.06	2935	3	7.34	1763	12	3.3	145	3	
	.024	0	7.13	7.0	2.9	.800	0.1	0.7	1E+10	14	12.78	6	1	8.42	149	6	5.6	27	2	
		100	7.09	6.9	2.6	.410	0.4	-1.4	2E+12	23	10.62	809	2	7.67	630	9	4.3	63	2	
		200	7.02	0.0	0.0	.136	1.2	-2.6	3E+13	31	8.24	19271	3	7.17	2631	14	3.4	213	3	
	W (3.5)	0	0	7.32	1.1	0.2	.921	0.3	2.1	1.0E+09	10	12.74	1	1	8.52	206	6	7.7	0.1	1
			100	7.31	1.1	0.1	.719	1.8	-0.4	3E+11	19	11.32	279	2	7.71	1299	11	6.5	0.2	1
			200	7.33	0.9	0.1	.477	6.7	-1.3	2E+12	24	10.35	2644	3	7.37	2964	14	5.6	0.7	1
.003		0	7.29	1.7	0.2	.891	0.2	1.6	3E+09	11	13.34	3	1	8.45	236	6	7.8	0.1	1	
		100	7.26	1.7	0.2	.630	1.4	-0.7	5E+11	20	11.10	466	2	7.68	1366	11	6.2	0.6	1	
		200	7.24	1.7	0.2	.383	2.9	-1.5	4E+12	25	10.18	4070	3	7.36	2973	14	5.4	1.4	1	
.024		0	7.04	8.6	0.9	.800	0.1	0.7	3E+10	14	12.67	12	1	8.36	296	7	7.3	0.5	1	
		100	7.04	8.7	0.8	.410	0.6	-2.1	1E+13	29	9.63	9992	3	7.45	2413	13	6.7	3.1	1	
		200	7.03	0.0	0.0	.136	1.1	-3.0	1E+14	37	8.97	63206	4	7.12	5063	17	6.0	6.5	1	

Thus, the chosen minerals were separated into their components activities as follows:

DCP	$\text{CaHPO}_4$	$(\text{Ca})(\text{H})(\text{P})$	$g_{\pm} = (\text{SAC})^{1/3}$
OCP	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$	$(\text{Ca})^4(\text{H})(\text{P})^3$	$g_{\pm} = (\text{SAC})^{1/8}$
HA	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	$(\text{Ca})^5(\text{P})^3(\text{H})$	$g_{\pm} = (\text{SAC})^{1/9}$
Bob	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$(\text{Mg})^3(\text{P})^2$	$g_{\pm} = (\text{SAC})^{1/5}$

where  $g_{\pm}$  is the mean ionic activity coefficient.

The results of these computations are listed in Tables 9 and 10.

## DISCUSSION

Treatment and Interpretation of Results

## Fixed Ionic Strength

## 1) No Addition of P

- At 0.00 mg/kg soil added P, the comparison of IAP to  $K_{sp}$  shows that all soils are supersaturated towards hydroxyapatite ( $pIAP < pK_{sp}$ ) and most undersaturated towards octocalcium, dicalcium and bobierite ( $pIAP > pK_{sp}$ ). Soils T1, T2, and T8 show a IAP/ $k_{sp}$  ratio between 0.1 and 1.0 for both octocalcium and dicalcium. This range is considered as a confirmation of a mineral controlling the concentration of an ion in the soil solution (Bohn and Bohn, 1987).

As pointed out by Bohn (1990), it is not required that "these minerals exist as such in the soils", the  $K_{sp}$ s are "used as reference states" and "the choice of the reference substance" as well as "of the value of its  $K_{sp}$  would improve the values of the activity coefficients".

Taking this into consideration, it appears for this study, that octocalcium is the best choice among Ca phosphates, not only because the IAPs were the closest to the  $K_{sp}$  of octocalcium, but also because the lowest ionic solid activity coefficients were obtained (Table 9).

- The total P concentration in the solid phase appears to influence the phosphate concentration in the solution phase (Table 8). In fact, a linear regression between these two variables for the 10 soils presented a  $r^2$  coefficient of 0.925 and if we consider only the Ponta soils, (same series) we get  $r^2 = 0.937$ .

This concentration dependency goes against the solubility product principle and seems to indicate the need for additional theoretical considerations. The solid solution theory can provide some light.

This concentration dependency is also reflected in the SAC, yielding a  $r^2$  coefficient of 0.900 for all soils and  $r^2 = 0.938$  for Ponta soils.

Equation (2)  $IAP = g X K_{sp}$ , indicates that an increase in X affect IAP. The results show a higher increase in IAP than the one expected to come from the increase in X. This lead to the calculation of a higher SAC.

The question now is: was there a real increase in SAC or was there not enough time for the state of partial equilibrium to be reached?

SAC is a measurement of non ideality; non ideality is due to constraints and strengths of electrostatic interactions. Hence, if SAC really went up it would have meant that the increase of P content in the solid phase was accompanied by a disruption in stability. This is a reasonable assumption that will be substantiated as we progress in this discussion.

- The level of fertilization of the ten soils is not the same. Tarrafal soils were taken from an experimental area where soils T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> and T<sub>8</sub> are cultivated most of the time fertilized whereas soils T<sub>5</sub> and (T<sub>6</sub>) are not. There is no history of heavy fertilization on soils A to D and Soil W is virgin.

Considering soils T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> and T<sub>5</sub> as belonging to the same series (see Table 1), the levels of total-P may be associated with increasing levels of fertilization.

- The ionic solid activity coefficients of phosphates in these basaltic soils are very low if compared with values calculated in the literature, reported by Bohn (1990) as being  $> 20$ . Fu-Yong and Bohn (1990) found phosphate ionic solid activity coefficients in acid soils to be  $> 10$ .

When octocalcium phosphate is used as reference, the ionic solid activities of the ten soils go from 1 to 4. The following considerations may constitute an explanation for these apparently low coefficients:

- i) Basaltic soils form mostly from extrusive igneous rocks. These rocks contain minerals formed from lava at high temperatures, which have cooled down quickly (volcanic activity) with limited or no time for selective crystallization. Therefore, many are amorphous, bearing a high degree of solid mixing. The amorphous components might be the closest thing to a pure solid solution, in Nature. Indeed, conditions for their formation, not only favored homogeneous mixing but also ideal mixing; Orville (1972), as indicated by Bohn (1990) found out that minerals mix ideally over a wide composition range, at high temperatures and pressure. It has been stressed many times in solid solution theory, that the higher the degree of homogeneity in the solid solution, the lower the SAC would be, which can be one explanation to these low coefficients.

- ii) Basaltic rocks contain high levels of ferromagnesian minerals, which are also Nesosilicates and Inosilicates. The sharing of oxygen

between silica tetrahedra is less in these silicates, leading to lower bonding energies. Lower bonding energies are due to fewer bonds and because bonding between common base ions and oxygen is weaker than bonding between Si and O. As a result, constraints and electrostatic forces are weaker than in granitic minerals, leading to lower solid activity coefficients (closer to ideality).

iii) A third reason why ionic solid activity coefficients are low in these soils may be linked to the assumption that the activity of the  $O^{2-}$  ion is one. This was based on the relative abundance of this ion in the solid. Basaltic materials contain higher levels of oxygen than granitic materials. Therefore the stated assumption bears more weight in this case.

iv) Volcanic soils are very sorptive, specially for phosphates, as can be observed in this research (around 90%) and throughout the literature: Moody and Radcliffe (1986) report adsorptions as high as 99%. High sorptivity means that bonds of surface oxide ions are not satisfied leading to stronger interaction of sorbate ions, "enough to be mixing homogeneously with the solid" (Bohn, 1990).

## 2) Effect of Adding P to the Suspensions

● When increasing amounts of P are added to the suspensions, the level of soluble P increases as well as the IAP (decrease of  $pIAP$  in Table 9). This trend is more accentuated in the non fertilized soils (Ts, A to W).

The increase in added P is also reflected in the SAC through linear equations of the type  $\log \text{SAC} = B(\text{added P}) + A$  as can be seen in Figs. (1, 2, 3 and 4).

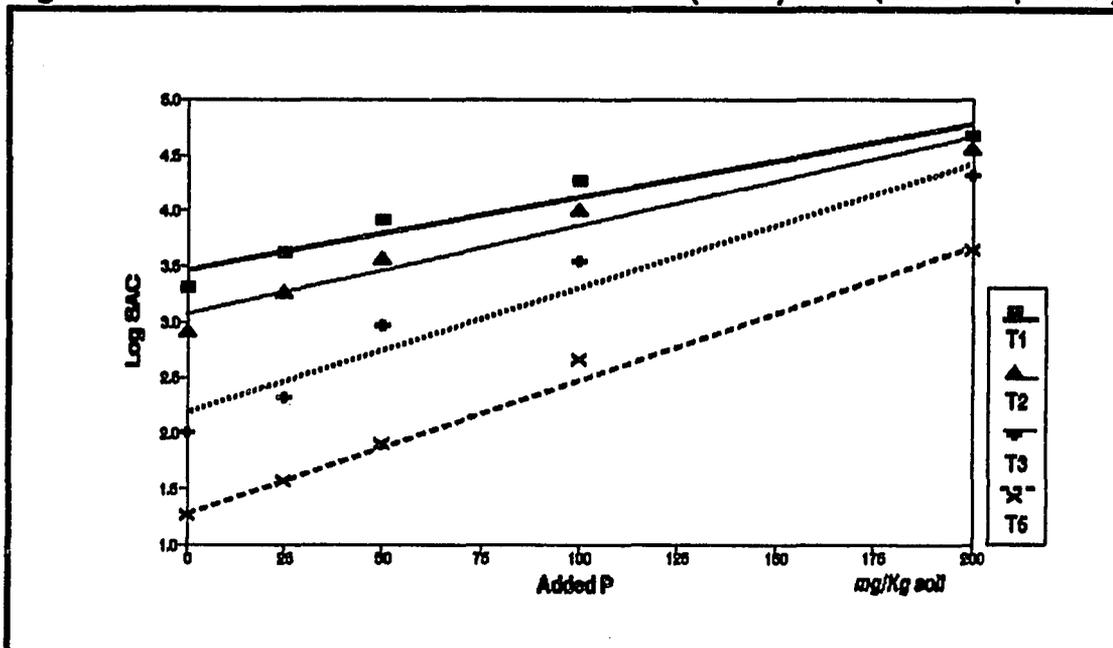
This kind of variation was found in acid soils by Fu-Yong and Bohn (1990). These authors admitted the possibility of an explanation by lack of equilibrium but believe that "decreased activity was a better and more satisfying explanation".

● The less fertilized soils (T<sub>3</sub> and T<sub>5</sub>) of the Ponta series, present higher slopes of the  $\log \text{SAC} = f(\text{added P})$  curves and their levels of SAC at 200 mg/kg P<sub>added</sub> are near the SAC levels of the fertilized soils at zero mg/kg P added. (Fig. 1). Blanchar and Stearman (1985) also found, in similar curves, a higher slope for non fertilized soils. This appears to be one reason for the interpretation of the higher total P level as due to fertilization. Figs. 3 and 4 (which compare the curves obtained with different minerals as reference) when juxtaposed show all curves as a continuum from Fig. 3 (the non fertilized soil T<sub>5</sub>) to Fig. 4 (the fertilized soil T<sub>1</sub>). It is as if soil T<sub>1</sub> had kept 200 mg/kg of added P from the past.

● As P is added, the IAP calculated with DCP as reference approaches the  $K_{sp}$  of this mineral at a slower pace than the IAP calculated with OCP as reference approaches the  $K_{sp}$  of octocalcium. This is reflected on the variation of the SAC with added P and can be seen in Figs. 3 and 4.

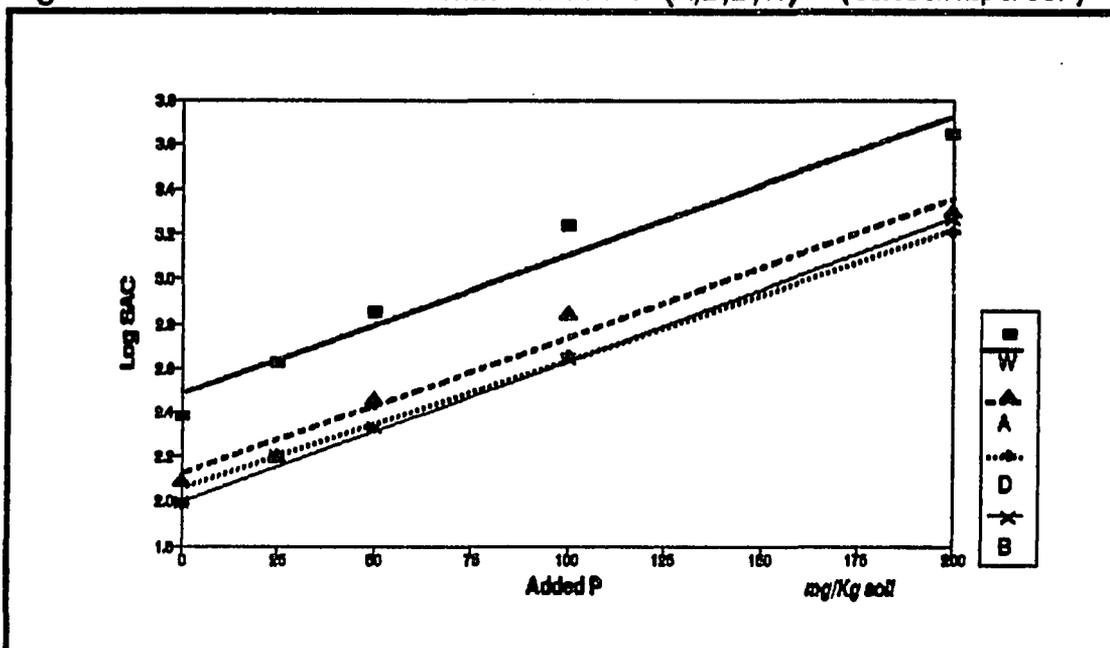
The result of the trend is more dramatic in Fig. 3, for the non fertilized soil, where the two curves cross each other, apparently suggesting an inversion in the order of precipitation.

Figure 1 : Variation of SAC with Added P (T1-T5) (Based on Kep of OCP)



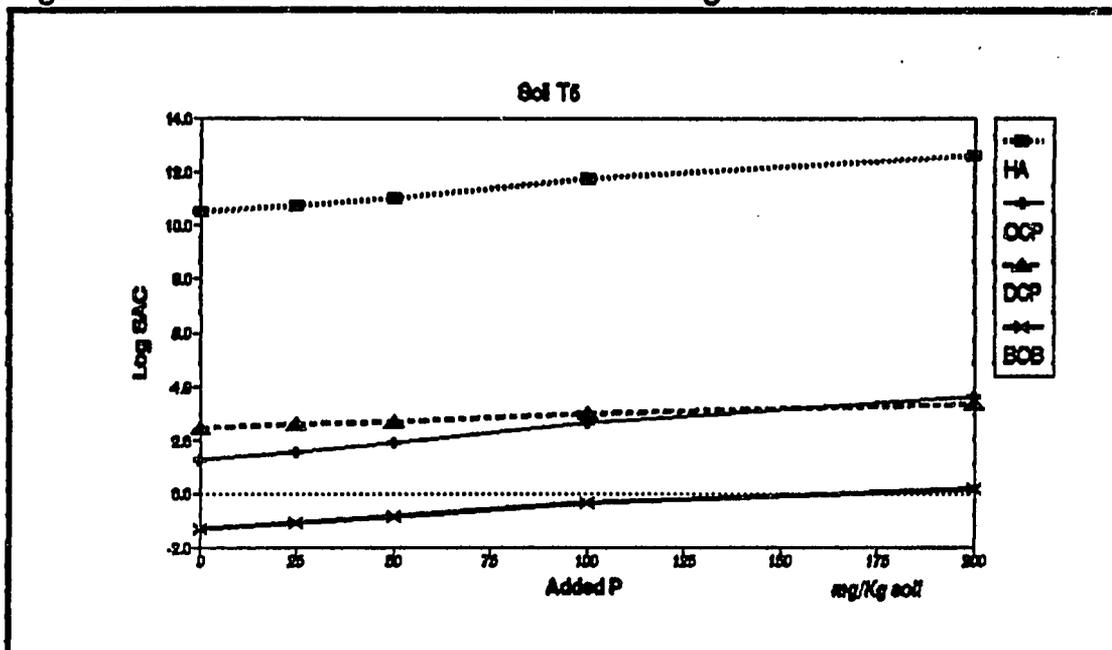
Soil	Added P	Log SAC	Linear Regression	r2
T1	0	3.30	$\text{Log (SAC)} = 0.0066 (\text{Added P}) + 3.46$	0.938
	25	3.62		
	50	3.92		
	100	4.27		
	200	4.68		
T2	0	2.93	$\text{Log (SAC)} = 0.0080 (\text{Added P}) + 3.07$	0.964
	25	3.27		
	50	3.57		
	100	4.01		
	200	4.57		
T3	0	2.01	$\text{Log (SAC)} = 0.0115 (\text{Added P}) + 2.16$	0.981
	25	2.33		
	50	2.97		
	100	3.55		
	200	4.32		
T5	0	1.27	$\text{Log (SAC)} = 0.0120 (\text{Added P}) + 1.31$	0.991
	25	1.58		
	50	1.91		
	100	2.67		
	200	3.64		

Figure 2: Variation of SAC with Added P (A,B,D,W) (Based on Ksp of OCP)



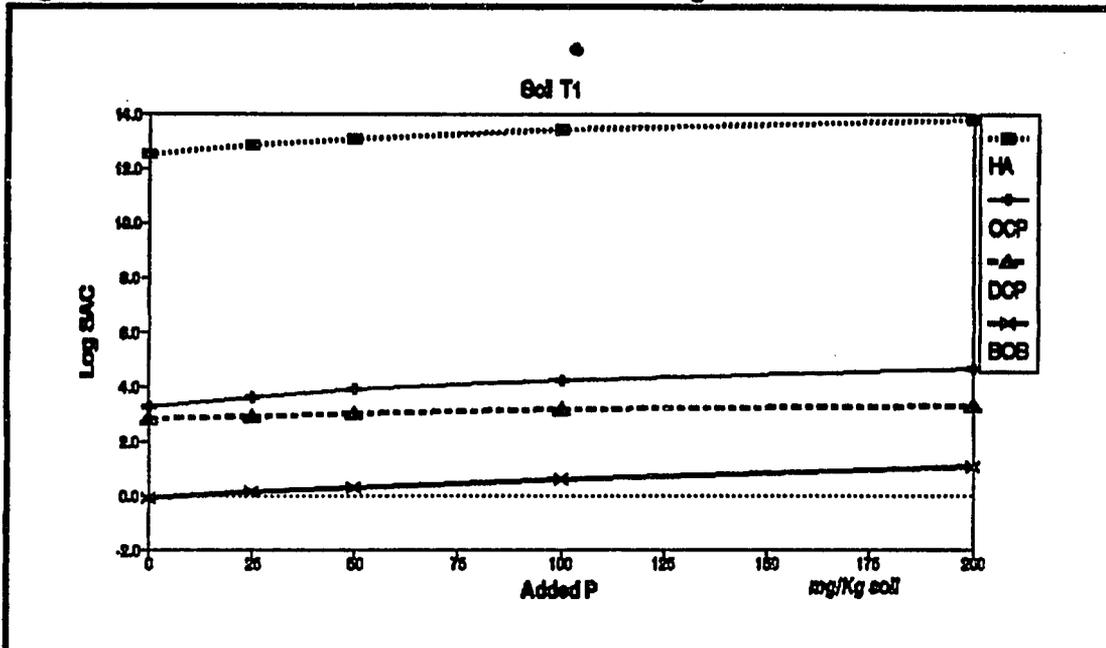
Soil	Added P	Log SAC	Linear Regression	r2
A	0	2.09	$\text{Log (SAC)} = 0.0062 (\text{Added P}) + 2.12$	0.977
	25	2.20		
	50	2.46		
	100	2.85		
	200	3.30		
B	0	1.99	$\text{Log (SAC)} = 0.0063 (\text{Added P}) + 2.02$	0.999
	25	2.20		
	50	2.33		
	100	2.65		
	200	3.26		
D	0	1.99	$\text{Log (SAC)} = 0.0059 (\text{Added P}) + 2.06$	0.986
	25	2.20		
	50	2.44		
	100	2.66		
	200	3.21		
W	0	2.38	$\text{Log (SAC)} = 0.0062 (\text{Added P}) + 2.48$	0.964
	25	2.63		
	50	2.86		
	100	3.24		
	200	3.65		

Figure 3: Variation of SAC with Added P Using Each Mineral as Reference



Mineral	Added P mg/Kg	Log SAC	Linear Regression	r <sup>2</sup>
HA	0	10.54	$\text{Log (SAC)} = 0.0106 (\text{Added P}) + 10.54$	0.989
	25	10.74		
	50	11.04		
	100	11.75		
	200	12.60		
OCP	0	1.27	$\text{Log (SAC)} = 0.0120 (\text{Added P}) + 1.31$	0.991
	25	1.58		
	50	1.91		
	100	2.67		
	200	3.64		
DCP	0	2.47	$\text{Log (SAC)} = 0.0045 (\text{Added P}) + 2.50$	0.991
	25	2.61		
	50	2.74		
	100	3.00		
	200	3.37		
BOB	0	-1.32	$\text{Log (SAC)} = 0.0075 (\text{Added P}) - 1.24$	0.972
	25	-1.08		
	50	-0.83		
	100	-0.34		
	200	0.17		

Figure 4 : Variation of SAC with Added P Using Each Mineral as Reference



Mineral	Added P mg/Kg	Log SAC	Linear Regression	r <sup>2</sup>
HA	0	12.55	$\text{Log (SAC)} = 0.0060 (\text{Added P}) + 12.71$	0.933
	25	12.97		
	50	13.10		
	100	13.45		
	200	13.81		
OCP	0	3.30	$\text{Log (SAC)} = 0.0066 (\text{Added P}) + 3.46$	0.938
	25	3.62		
	50	3.92		
	100	4.27		
	200	4.69		
DCP	0	2.63	$\text{Log (SAC)} = 0.0024 (\text{Added P}) + 2.89$	0.940
	25	2.93		
	50	3.05		
	100	3.18		
	200	3.33		
BOB	0	-0.08	$\text{Log (SAC)} = 0.0057 (\text{Added P}) - 0.00$	0.981
	25	0.14		
	50	0.33		
	100	0.64		
	200	1.08		

However, we should remember that, the choice of the reference mineral does not change the physical data, only manipulates them in different ways. By changing minerals we vary the proportion of ions in the computation of IAP. As a mathematical consequence the dependant variables (IAP, SAC) would change at different rates when small changes in the independent variable (  $P_{added}$  ) are made.

Consequently, the ionic solid activity coefficient has more meaning because it levels these discrepancies by extracting the  $n$  root of the SAC,  $n$  being the number of times the activity of ions enter in the IAP as a factor. And this ionic activity coefficient grows in a faster pace when calculated for DCP than for OCP. In addition, the ionic solid activity under DCP is higher than under OCP, particularly at 200 mg/kg of P added where it may reach levels of 16 vs. 3 under OCP (soil W).

● The IAPs calculated for bobierrite are well below the  $K_{sp}$  of that magnesium phosphate, indicating complete dissolution of the mineral if present. In fact, magnesium phosphates have been reported as too soluble substances to be important in soils (Lindsay, 1979). However, this author do not discard the possibility of magnesium phosphate formation in soils and refers to magnesium phosphates as having been found in soils as initial reaction products of phosphate fertilizers (Lindsay 1979).

This possibility is not remote for the studied soils, despite the low IAP values encountered, when the solid solution theory is considered: if magnesium phosphates are being formed as solid solutions their SAC would decrease in such a way that the reduced escaping tendency would

prevent levels of magnesium and phosphate ions in solution to be near the  $K_{sp}$ s of the correspondent pure minerals. A way of preventing such levels would be sorption at the surface as solid solutions.

Indeed, SAC and ionic solid activity coefficients calculated for bobierrite in these soils show very low values, compatible with the solid solution theory.

The following considerations would favor the hypothesis of magnesium phosphates solid solution possible formation:

i) As said before, basaltic materials are rich in ferromagnesian minerals. Hence, there is no lack of Mg ions in the system.

ii) The availability of attachment sites is probably high because Mg-O bonds are weak, high rates of P adsorption have been observed and the concentration of Mg increased easily in solution when Ca was added.

#### Effect of Calcium Addition

##### 1) No Addition of P

• When Ca was added to the suspensions the level of soluble P decreased. The reason for this decrease is linked to the increase of ionic strength as explained by Bar-Yosef et al. (1988).

These authors found in various adsorption experiments that variation of I.S. within the E.C. range of 2 to 5 dS/m could induce considerable variability in the concentration of soluble P. The decrease of this concentration represents an increase in adsorption, which goes against the fact that the "effect of I.S. on activity coefficients should induce a diminished adsorption with elevated I.S.". (Bar-Yosef et al., 1988). The same authors go on explaining that increased I.S. limits the

extent of the diffuse double layer, reducing the masking of P adsorption sites. They also report same effects when Ca rather than K is used.

• The plot for the variation of Log SAC with added Ca (Fig. 5) present curves with some degree of linearity. We should expect a decrease in SAC with increasing Ca since data show a corresponding increase in adsorption. In addition, these curves do not follow the theory of Bar-Yosef et al presented above (except soil A).

The reason for those discrepancies is because octocalcium was used as reference, hence incorporating the increase of  $(Ca^{++})$  in the computation of IAP and SAC. The higher  $(Ca^{++})$  masks the influence of increased ionic strength on SAC.

In order to account for the effect of I.S. (according to the observations and explanations of Bar-Yosef) we should redraw the curves based on the  $k_{sp}$  of bobierrite, since  $(Ca^{++})$  does not enter in the IAP calculation. The results of this recalculation are presented in Fig. 6.

The "considerable decrease in the concentration of soluble P" ( $\Rightarrow$  increase in adsorbed P  $\Rightarrow$  decrease in SAC) starting between EC = 2 dS/m and 5 dS/m is verified: 0.009 mol/L gave a EC reading of 2.19 dS/m and 0.024 mol/L corresponds to a 5.43 dS/m (Table 8) where the effect is no longer felt and the increase in  $(Mg^{++})$  takes its course in the shaping of the SAC curve (notice the slope as being the same as in the beginning of the plot). Owing to the scarcity of measured points, curves in Figure 6 appear polygonal when they should have been smooth and present inflections at a point between 0.003 mol/L and 0.009 mol/L, and at a point before 0.024 mol/L.

Figure 5: Variation of SAC with Added Ca (Based on Ksp of OCP)

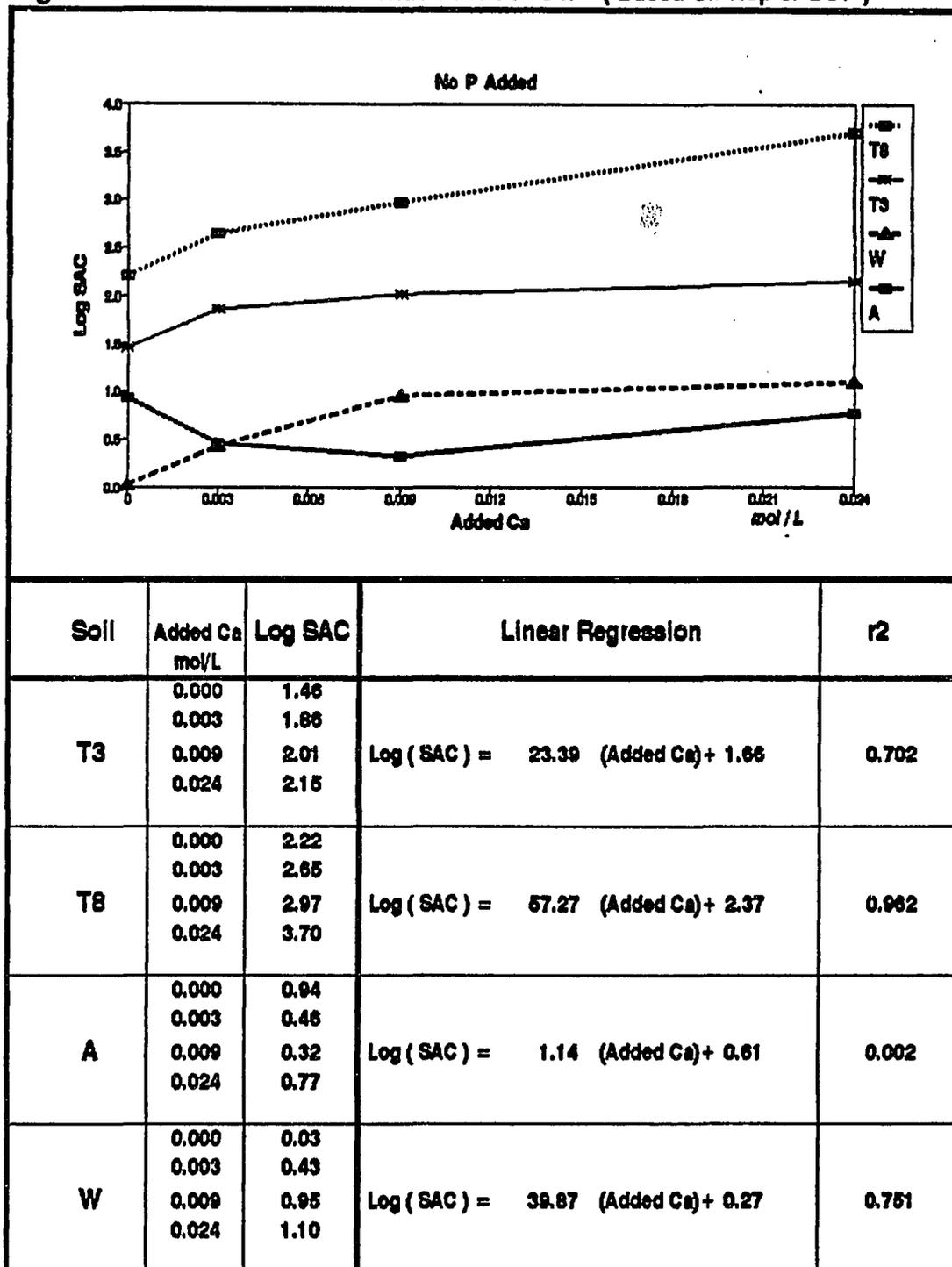
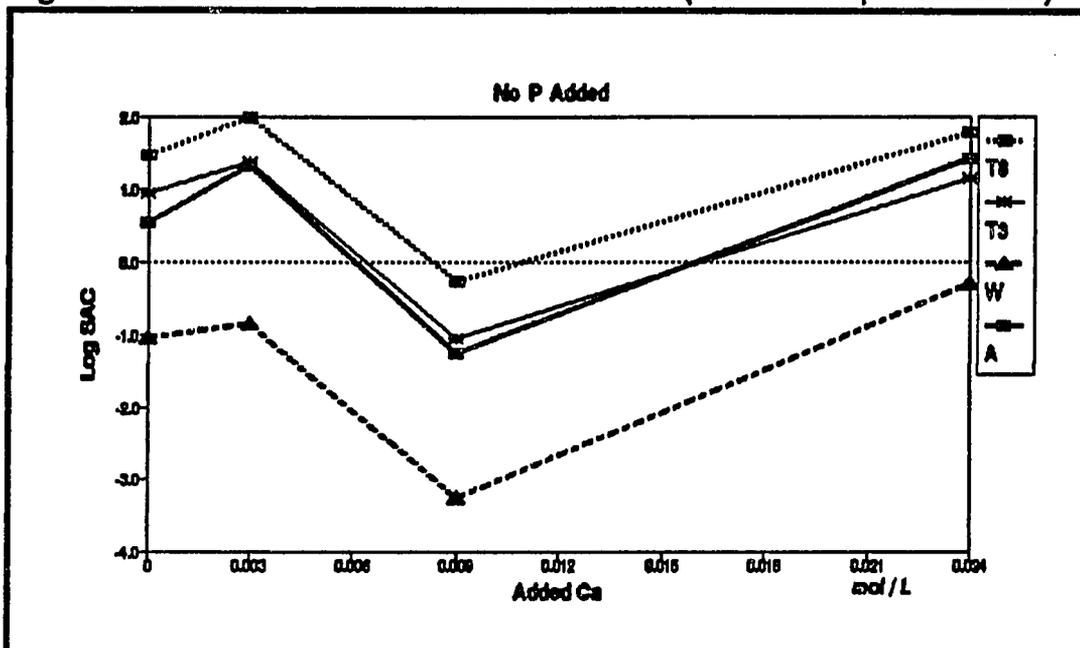
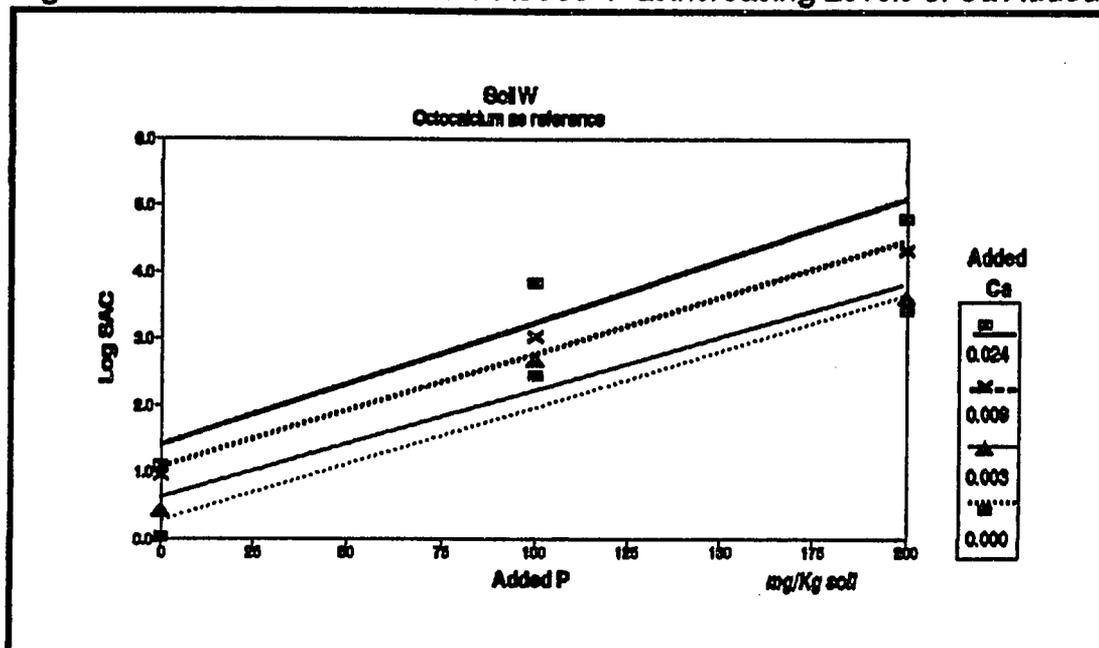


Figure 6: Variation of SAC with Added Ca (Based on Ksp of Boblerrite)



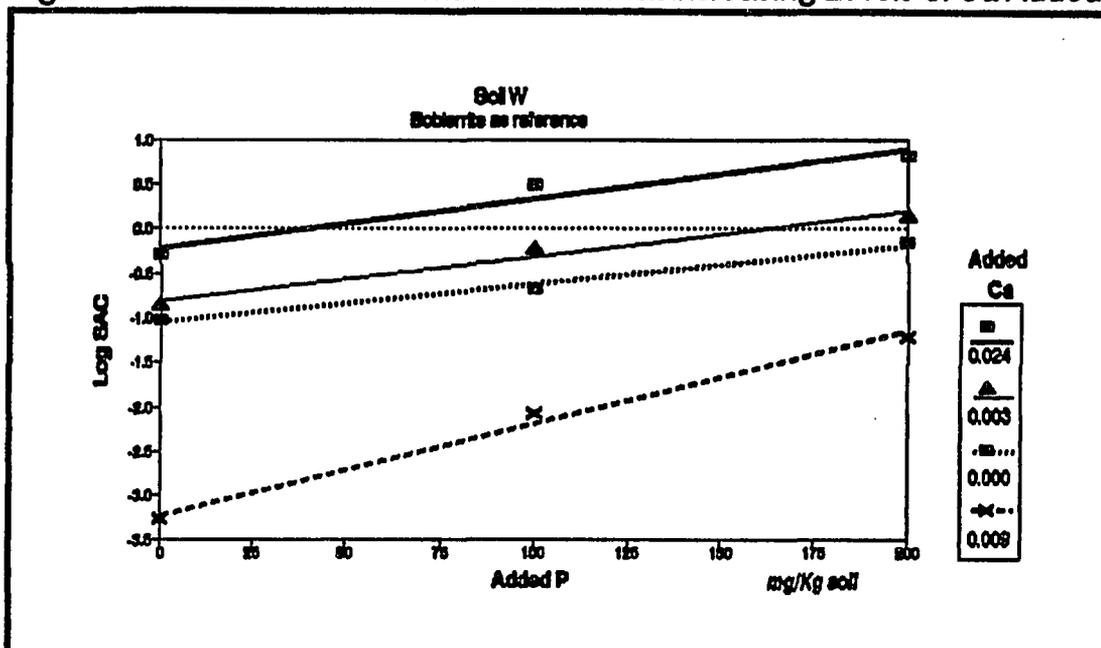
Soil	Added Ca mol/L	Log SAC	Linear Regression	r <sup>2</sup>
T3	0.000	1.0	$\text{Log (SAC)} = 1.67 (\text{Added Ca}) + 1.370$ Not Linear	0.000
	0.003	1.4		
	0.009	-1.0		
	0.024	1.2		
T8	0.000	1.5	Not Linear	0.000
	0.003	2.0		
	0.009	-0.3		
	0.024	1.8		
A	0.000	0.5	Not Linear	0.000
	0.003	1.3		
	0.009	-1.3		
	0.024	1.4		
W	0.000	-1.0	Not Linear	0.000
	0.003	-0.9		
	0.009	-3.3		
	0.024	-0.3		

Figure 7: Variation of SAC with Added P at Increasing Levels of Ca Added



Added Ca mol/L	Added P mg/Kg	Log SAC	Linear Regression	r <sup>2</sup>
0	0 100 200	0.0 2.4 3.4	$\text{Log (SAC)} = 0.0170 (\text{Added P}) + 0.27$	0.943
0.003	0 100 200	0.4 2.7 3.6	$\text{Log (SAC)} = 0.0159 (\text{Added P}) + 0.64$	0.947
0.009	0 100 200	0.9 3.0 4.3	$\text{Log (SAC)} = 0.0169 (\text{Added P}) + 1.08$	0.982
0.024	0 100 200	1.1 3.6 4.6	$\text{Log (SAC)} = 0.0185 (\text{Added P}) + 1.39$	0.929

Figure 8 : Variation of SAC with Added P at Increasing Levels of Ca Added



Added Ca mol/L	Added P mg/Kg	Log SAC	Linear Regression	r <sup>2</sup>
0	0	-1.0	Log (SAC) = 0.0044 (Added P) -1.05	0.990
	100	-0.7		
	200	-0.1		
0.003	0	-0.9	Log (SAC) = 0.0050 (Added P) -0.61	0.977
	100	-0.2		
	200	0.1		
0.009	0	-3.3	Log (SAC) = 0.0103 (Added P) -3.22	0.991
	100	-2.1		
	200	-1.2		
0.024	0	-0.3	Log (SAC) = 0.0055 (Added P) -0.22	0.947
	100	0.5		
	200	0.8		

## 2) Addition of P

Different levels of added Ca do not affect the linearity of the variation of log SAC with added P. This can be illustrated in Figures 7 and 8.

Figures 7 and 8, where the virgin soil W was chosen, also show the influence of I.S. on SAC as pointed out before: The intercepts of the curves grow with increasing levels of added Ca when octocalcium is used as reference. However, when bobierrite is used, we notice the "fall" of the 0.009 mol/L curve way below the other ones (Fig. 8). The regression coefficients also improved when bobierrite was used as reference.

### Adsorption Isotherms

#### 1) Langmuir

The following form of the Langmuir equation was applied to the data:

$$\frac{C}{x/m} = \frac{1}{bV_m} + \frac{C}{V_m} \quad (13)$$

where C is the equilibrium P concentration,  $x/m$  is the amount of P adsorbed per unit mass of adsorbent,  $V_m$  is the P adsorption maximum and b is a constant related to the energy of adsorption (Table 11). Not only was curvature found but also the scatter of data due to analytic error in the determination of P at low concentrations was amplified.

Another problem was that for some soils  $x/m$  was increasing in a faster pace than the amount  $C$  left in solution yielding a decreasing curve (Figure 9).

In order to solve those problems a second form of the Langmuir equation was used, despite the advice of Thomas and Thomas (1967), who consider that "too much weight is placed on the low-concentration portion of the isotherm" (White and Zelazny, 1986):

$$\frac{V_m}{x/m} = \frac{1}{bC} + 1 \quad (14)$$

The data were scattered and increasing  $PO_4$  caused nonlinearity (Figure 9).

## 2) Freundlich

The form of Freundlich equation modified by Low and Black (1950) was tried:

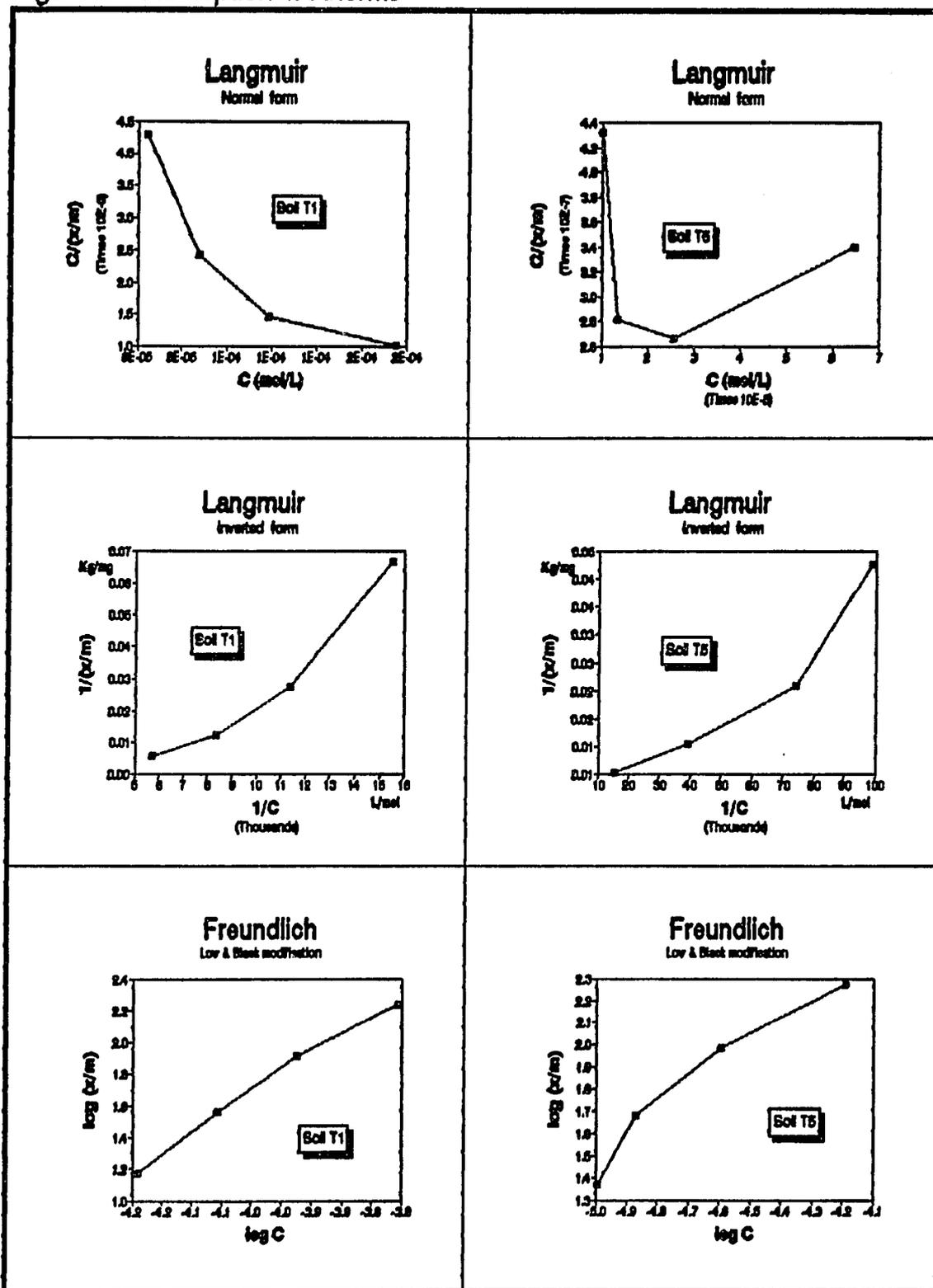
$$\log x/m = \log k' + \frac{1}{n} \log C \quad (15)$$

This equation also gave improved results (Figure 9).

Table 11: Calculation of Adsorption Isotherms

Added P	P in solution		Langmuir				Freundlich (Low & Black modification)		
	mg/Kg soil	C mol/L	Normal		Inverted		log C	log x/m	
			x/m	C/(x/m)	1/(x/m)	1/C			
T1	25	10	6.45E-05	15	4.30E-06	0.057	1.55E+04	-4.19	1.18
	50	14	8.81E-05	36	2.42E-06	0.028	1.13E+04	-4.05	1.56
	100	18	1.19E-04	82	1.46E-06	0.012	8.40E+03	-3.92	1.91
	200	27	1.75E-04	173	1.02E-06	0.006	5.70E+03	-3.76	2.24
T2	25	8	4.87E-05	17	2.79E-06	0.057	2.05E+04	-4.31	1.24
	50	10	6.45E-05	40	1.61E-06	0.025	1.55E+04	-4.19	1.50
	100	15	9.53E-05	85	1.16E-06	0.012	1.02E+04	-4.01	1.83
	200	25	1.59E-04	175	5.09E-07	0.005	5.28E+03	-3.80	2.24
T3	25	2	1.46E-05	23	6.44E-07	0.044	6.83E+04	-4.83	1.36
	50	4	2.43E-05	46	5.26E-07	0.022	4.11E+04	-4.61	1.66
	100	6	4.09E-05	94	4.37E-07	0.011	2.45E+04	-4.39	1.97
	200	13	8.11E-05	187	4.33E-07	0.005	1.23E+04	-4.09	2.27
T6	25	2	1.01E-05	23	4.32E-07	0.043	9.87E+04	-4.99	1.37
	50	2	1.33E-05	46	2.82E-07	0.021	7.41E+04	-4.87	1.55
	100	4	2.56E-05	96	2.67E-07	0.010	3.91E+04	-4.59	1.85
	200	10	6.45E-05	190	3.40E-07	0.005	1.55E+04	-4.19	2.28
T8	25	7	4.40E-05	18	2.42E-06	0.055	2.28E+04	-4.36	1.26
	50	9	5.72E-05	41	1.39E-06	0.024	1.75E+04	-4.24	1.61
	100	12	7.69E-05	88	8.99E-07	0.011	1.27E+04	-4.10	1.94
	200	26	1.70E-04	174	9.77E-07	0.006	5.89E+03	-3.77	2.24
A	25	1	4.77E-06	24	1.96E-07	0.041	2.10E+05	-5.32	1.38
	50	1	9.03E-06	49	1.86E-07	0.021	1.11E+05	-5.04	1.69
	100	3	2.18E-05	97	2.26E-07	0.010	4.58E+04	-4.66	1.99
	200	10	6.45E-05	190	3.40E-07	0.005	1.55E+04	-4.19	2.28
B	25	0	2.70E-06	25	1.10E-07	0.041	3.71E+05	-5.57	1.39
	50	1	3.73E-06	49	7.54E-08	0.020	2.69E+05	-5.43	1.69
	100	1	7.95E-06	99	8.05E-08	0.010	1.26E+05	-5.10	1.99
	200	5	3.37E-05	195	1.73E-07	0.005	2.97E+04	-4.47	2.29
C	25	0	2.70E-06	25	1.10E-07	0.041	3.71E+05	-5.57	1.39
	50	1	3.73E-06	49	7.54E-08	0.020	2.69E+05	-5.43	1.69
	100	1	7.95E-06	99	8.05E-08	0.010	1.26E+05	-5.10	1.99
	200	5	3.09E-05	195	1.58E-07	0.005	3.24E+04	-4.51	2.29
D	25	0	2.70E-06	25	1.10E-07	0.041	3.71E+05	-5.57	1.39
	50	1	4.77E-06	49	9.67E-08	0.020	2.10E+05	-5.32	1.69
	100	1	7.95E-06	99	8.05E-08	0.010	1.26E+05	-5.10	1.99
	200	4	2.82E-05	196	1.44E-07	0.005	3.54E+04	-4.55	2.29
W	25	1	4.77E-06	24	1.96E-07	0.041	2.10E+05	-5.32	1.38
	50	1	9.03E-06	49	1.86E-07	0.021	1.11E+05	-5.04	1.69
	100	4	2.43E-05	96	2.53E-07	0.010	4.11E+04	-4.61	1.98
	200	9	5.08E-05	191	3.19E-07	0.005	1.64E+04	-4.22	2.28

Figure 9: Adsorption Isotherms



Further Theoretical Considerations

Surface-P vs. Total-P

● Blanchar and Stearman (1984, 1985) employed a different formulation of the solid-solution equation as well as calculated the mole fraction differently. They derived their equations from the one given by Garrels and Christ (1965):

$$\log g = B'(1-m)^2 \quad (16)$$

where  $g$  is the solid activity coefficient,  $B'$  a constant and  $m$  the molar fraction. This molar fraction was defined as  $P_{\text{added}}/PS_{\text{max}}$  ( $PS_{\text{max}}$  is the maximum amount of P which the soil can adsorb). The derivation yields:

$$\ln P = A + B(PS) + C(PS)^2 \quad (17)$$

whose constants were determined by data fitting; ( $PS$  means sorbed P and P is phosphorus in solution). Those constants allowed the determination of  $P_{\text{max}}$  and  $PS_{\text{max}}$  which were used to make linear plots  $\ln [P]$  vs  $(1 - [PS]/[PS_{\text{max}}])^2$ . The linearity of these plots "were used to test P sorption conformity to regular solid-solution concepts". (Blanchar and Stearman, 1985).

● The formulation  $\log SAC = A + B(P_{\text{added}})$  used by Fu-Yong and Bohn (1990) and in this research, may also be derived from equation (16) as follows

$$\log SAC = B' \left(1 - \frac{P_{\text{added}}}{PS_{\text{max}}}\right)^2 = B' - 2B' \left(\frac{P_{\text{added}}}{PS_{\text{max}}}\right) + B' \left(\frac{P_{\text{added}}}{PS_{\text{max}}}\right)^2$$

with  $g = SAC$  and  $m = P_{\text{added}}/PS_{\text{max}}$

If we consider  $(P_{\text{added}}/PS_{\text{max}})$  as negligible, the square term can be dropped and we get

$$\log SAC = B' - \frac{2B'}{PS_{\text{max}}} (P_{\text{added}})$$

making  $B' = A$  and  $-2B'/PS_{\text{max}} = B$  (since  $PS_{\text{max}}$  is constant for a given soil); we get finally

$$\log SAC = A + B (P_{\text{added}})$$

Therefore, the equation used in this work is of the same kind as the one derived by Blanchar and Stearman. It should present however a curvature at high levels of added P because it lacks the square term.

- Blanchar and Stearman state that their model is based on the assumption that a P molecule when adsorbed alters the energy available for further adsorption of P on adjacent sites. This agrees with the g term which represents a deviation from ideality and accounts for the "excess free energy" as stated before (Denbigh, 1971).

- Thomas and Thomas (1967) point out that the Freundlich equation was derived to allow a logarithmic decrease in adsorption energy with increasing coverage. It appears that a Freundlich type of equation, the Blanchar and Stearman equation and the one used in this research (as well as by Fu-Yong and Bohn) are mathematical translations of the same physical phenomenon.

- Is this phenomenon in conformity with the solid solution theory? Blanchar and Stearman believe P sorption behaves as predicted

for a regular solid-solution because they obtained a good fit of the data to eq. (17), constancy of  $B'$  and linearity of the plots.

Fu-Yong and Bohn (1990) on the same soils (furnished by Blanchar) also found linearity when they applied the simplified equation; however Bohn (1990) interprets phosphates in those soils as not behaving as solid solutions because the calculated activity coefficients were very large.

• The reason for this dilemma may reside on the definition of the mole fraction, as explained next:

Blanchar and Stearman consider only P on the surface of particles as controlling the activity of the solution, they determine mole fractions based on adsorbed P and adsorption maxima. Thus, by undergoing their experiments they have to measure quantities related only to newly adsorbed P (notice that no IAP is measured in equation 17) this newly adsorbed P is likely to behave like a solid-solution because:

1) solid surfaces, as a consequence of weathering, appear uniform to the ion, allowing it to mix homogeneously with other ions on the surface; 2) the linearity of those curves, which were derived from solid-solution formulation, is reasonable evidence; 3) at low concentrations the new forms will present low mole fractions as required for solid-solution behavior.

Fu-Yong and Bohn use mole fractions calculated from the total solid composition. As a consequence, P belonging to the "old" natural minerals is taken into account directly in X, and indirectly in IAP which represents the escaping tendency of P in the mineral. Certainly

the newly formed P is also considered in total P but the "old" minerals dominate, specially in virgin and non fertilized soils. Phosphates in these minerals do not have to behave as a regular solid solution, because they were probably formed under geological, not soil conditions. They may be present as pure crystals, physical mixtures, solid solutions or all of the above.

This may be the reason why SAC for phosphates are very large in the literature even if there is evidence of their behavior as solid-solutions. The soils used by Blanchar and Stearman, when given the Fu-Yong and Bohn treatment, presented high g values because phosphates in the minerals are not solid solutions. They yielded linear plots when P was added because the newly sorbed P likely was a solid-solution.

#### Solid-Solution and P Retention

The focus of these studies and of this particular research has been on tentative explanation for the high levels of P retention by soils. The solid-solution concepts state that the escaping tendency of an ion (in this case the phosphate ion) is decreased because entropy of mixing increases.

If the escaping tendency of an ion is decreased, meaning that it will not go to the aqueous solution as easily as it used to go when non homogeneously mixed, it means equally that it would "enter" in the solid-solution more easily than before. And that is an explanation for higher rates of sorption.

Hence, the higher the solid solution character of minerals in the soil, the higher P sorption will be. It was suggested in this study that

the reason why volcanic and basaltic soils present high levels of sorptivity, was because their minerals behave like solid solutions.

In sum, the nature of soil minerals may influence the behavior of ion sorption but do not determine it.

If the soil dries quickly, which is the case of these surface soils in isohyperthermic and thermic regimes, phosphates may have to form as coprecipitates or as low crystallized compounds (no time for ion segregation) which are also considered solid-solutions.

## SUMMARY AND CONCLUSIONS

The main goal of this research was to study the nature of P retention in alkaline soils from basalt following a solid-solution theory approach. A set of objectives was established in the Introduction and as a result of this study some answers were found relevant to those objectives.

Answers to the Objectives

1) 1<sup>st</sup> objective: Interpretation of SAC of calcium and magnesium phosphates as influenced by added P, added Ca, Ca and Mg activities.

- The SACs obtained when no P was added were low and compatible with solid-solution theory.

- The SAC obtained by adding increasing amounts of phosphates fits a linear plot of the type:  $\text{Log SAC} = B(P_{\text{added}}) + A$ .

- This linearity is evidence of solid-solution behavior.

- Adding Ca did not change the linearity of plots.

- There is an overall decrease in SAC when 0.009M of  $\text{CaCl}_2$  is used. Reason: effect of I.S. on the diffuse double layer.

- SACs calculated for magnesium phosphates suggest the possibility of their formation.

2) 2<sup>nd</sup> objective: Calculate the ionic solid activity coefficients of  $\text{PO}_4^{3-}$  on the above situations.

- The ionic solid activity coefficient for  $\text{PO}_4^{3-}$  was calculated as the mean activity coefficient using 4 different phosphates as reference and were smallest for octocalcium and bobierrite.

- They were lower than the ones found in the literature.

- This low values may be explained by the nature of minerals in basaltic soils.

3) 3rd objective: Consider other approaches related to the solid-solution treatment.

- Data do not fit Langmuir equations.

- A better fit was found for a form of the Freundlich equation.

- Equations used by Blanchar and Stearman where the mole fraction is linked to surface-P is of the same nature as the ones used in this research where the mole fraction is calculated with total-P.

### Conclusions

The most important conclusion is that phosphates in alkaline soils from basalt behave like solid-solutions. Other important conclusions follow:

- Phosphates retained at the surface of minerals probably behave like solid-solutions.

- When the entire solid composition is used in the computation of SAC, the solid-solution character of soil minerals may be assessed.

- This solid-solution character is better appreciated through ionic solid-solution coefficients than through salt SAC.

- There is no major difference on the application of solid-solution theory to soils at the encountered pH range (7.0 to 7.8) compared to studies on acid soils.

- Because SAC encountered in the literature for phosphates are very high compared to most weakly soluble ions and trace elements, we should not consider that phosphates can not behave in soils like solid-solutions.

- The high SAC encountered in the literature may be due to measurements done on the entire solid, which may not be a solid-solution.

- A non solid-solution mineral may not favor formation of new phosphates as solid-solution but do as not prevent such formation from taking place. The reason is because the assumption on the uniformity of solid surfaces is reasonable and because phosphates can coprecipitate as solid-solutions when the soil dries quickly.

- Basaltic soils present solid-solution behavior because most of their components are amorphous or weakly crystallized materials, bearing higher degrees of homogeneous mixing.

- They also present lower SAC than granitic soils because basaltic minerals have weaker molecular bonds.

- Because of the solid-solution nature of basaltic minerals, P sorption is high in these soils and the possibility for magnesium phosphate formation deserves to be considered.

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