ORTHO- AND PYROPHOSPHATE SORPTION EFFECTS ON ZINC TRANSFORMATIONS IN THREE QUEBEC SOILS

by

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A thesis submitted to
Faculty of Graduate Studies and Research
McGill University
in partial fulfillment of requirements for
the degree of Doctor of Philosophy

September, 1988

Suggested short title:

ORTHO- AND PYROPHOSPHATE SORPTION AND ZINC TRANSFORMATIONS IN SOILS

ABSTRACT

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Interactions of ortho- (OP) and pyrophosphates (PP) with Zn need to be quantified on agricultural soils. Three Quebec soils were equilibrated with OP or PP solutions, then with Zn solutions, and finally with solutions containing neither P nor Zn. Subsequently, Zn fractions were extracted sequentially with KNO_3 (Zn_{KNO3}), NaOH (Zn_{NaOH}) solutions and concentrated HNO_3+H_2O_2 (Zn_{HNO3}). Autoclaved soils were used for OP and PP comparisons, and non-autoclaved soils for OP determinations.

One mmole sorbed P resulted in increases in CEC from 0.52-1.24 mmole(+), and increased CEC per mmole sorbed P was greater with sorbed OP than with sorbed PP. Absolute increase in CEC was more with sorbed PP than with OP due to greater P sorption as PP. Sorbed OP or PP increased specific Zn sorption in association with soil oxide materials: (1) P sorption increased Zn sorption but reduced Zn desorption, (2) P sorption reduced KNO_3- but increased NaOH- and HNO_3- extractable Zn, and (3) P sorption increased the difference between Zn sorbed and Zn extracted with KNO_3. These effects were more significant in coarse than in fine textured soils, and greater with PP compared with OP.

RESUME

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La teneur en zinc assimilable des cultures est affectée par les interactions P-Zn dans le sol. Les additions d'orthophosphates (OP) peuvent diminuer ou n'avion aucun effect sur la solubilite du zinc alors que celles de pyrophosphates (PP) peuvent l'augmenter ou n'avion aucun d'effect. Les mecanismes impliqués dans les interactions ne sont pas bien compris et il est donc nécessaire de les quantifier pour les sols sujets à une fertilisation phosphatée.

Des echantillons pris en surface et en profondeur pour trois sols agricoles québequois furent mis en équilibre avec des solutions d'OP ou de PP, puis avec des solutions de Zn et finalement avec des solutions ne contenant ni P ni Zn. Le premier équilibre permit d'evaluer l'effet de l'adsorption du P sur la capacité d'échange cationique (CEC), le second, l'adsorption du Zn après celle du P, et la troisième la désorption du Zn en relation avec l'addition de P. Ensuite, une extraction séquentielle des fractions de Zn avec des solutions de KNO_3, NaOH et de $HNO_3+H_2O_2$ concentré fut faite. Des sols passés à l'autoclave furent utilisés pour comparaison de OP et PP, et des sols non autoclavés furent utilisés pour la determination de OP.

Le passage à l'autoclave a réduit grandement le fer et l'aluminium extractible au dithionite-citrate. Avec ou sans passage à l'autoclave, l'adsorption de 1 mmole de P (PP ou OP) par le sol a demontre une augmentation de la CEC de 0.52 à 1.24 mmole$^{(+)}$. La comparaison entre OP adsorbé et PP pour les sols passés à l'autoclave a montré que

l'augmentation de la CEC pour chaque mmole de P adsorbé était superieure pour OP comparee a PP malgré un taux similairé d'addition de P. L'augmentation en valeur absolue de la CEC était supérieure avec PP adsorbé compare a OP, probablement à cause d'une meilleure adsorption de P avec PP compare à OP.

L'adsorption de OP ou PP pour les sols passés à l'autoclave et l'adsorption de OP pour les sols non passés à l'autoclave montrèrent une augmentation spécifique d'adsorption de Zn en relation avec les oxydes. L'effet fut plus marqué avec PP qu'avec OP, tel que l'indiquent les observations suivantes: (1) L'adsorption de P montra une augmentation de l'adsorption de Zn et réduisit la désorption de Zn; (2) l'adsorption de P reduisit le Zn extractible au KNO_3 mais augmenta le Zn extractible au NaOH- ainsi qu'au HNO_3; et (3) l'adsorption de P augmenta la différence entre le Zn adsorbé et le Zn extrait avec KNO_3. Les effets furent plus significatifs dans les sols a texture grossière que ceux à texture fine. Les résultats suggerent que l'application de Zn doit être dissociée de celle de P pour éviter l'augmentation de l'adsorption de Zn et la diminution de la désorption de Zn.

PREFACE

Use of fertilizers for crop production is an almost universal process, yet is complicated by interactions among nutrients, soils and crops. Phosphorus (P) and zinc (Zn) interactions have been demonstrated in crop production and in soils, based on fertilizers containing orthophosphate (OP). Other fertilizer P carriers now in use include solutions of polyphosphate, of which the most common constituent is often pyrophosphate (PP). Solutions of PP have different properties than those of OP, including chelation of metal cations. Thus, the PP-Zn interactions may be entirely different than the OP-Zn interactions. The mechanisms of interactions between OP or PP and Zn needs to be determined in soils, and P-Zn effects on Zn reaction need to be quantified. An effort was made in the present study to investigate the mechanisms of OP- or PP-Zn interactions on Zn transformations in three agricultural soils, in order to understand potential P-Zn interactions in soils.

The dissertation is composed of four Chapters preceded by an Introduction and followed by a section of General Conclusions and Future Research. Chapter I, entitled "Literature Review", establishes the context of the study and generates hypotheses to be tested. Chapter II, entitled "Effects of Sorbed Orthophosphate on the Zinc Status in Three Soils of Eastern Canada", examines Zn transformations in soils treated with OP, and is accepted for publication in the Journal of Soil Science (1989, 40(1)), thus literature citations follow the format of the Journal of Soil Science. Chapter III, entitled "Effects of Sorbed Pyrophosphate on the Zinc Status of Three Autoclaved Soils of Eastern

Canada", evaluates Zn transformations in soils treated with PP, and is prepared for submission to the Soil Science Society of America Journal. Chapter IV, entitled "Comparisons of Sorbed Ortho- and Pyrophosphates on Zinc Reaction in Three Autoclaved Soils", discusses and compares mechanisms of OP-Zn or PP-Zn interactions in autoclaved soils, and is also prepared for submission to the Soil Science Society of America Journal. Connecting paragraphs have been inserted between Chapter II and Chapter III, and between Chapter III and Chapter IV. A paper entitled "The pH Effect on Sorption-desorption and Fractions of Zinc in Phosphate Treated Soils", published in Commun. Plant Sci. Soil Anal. 19: 873-886, comprises results related to this thesis, was presented as an appendix (APPENDIX II).

The following remark concerning the authorship of papers is exerpted from Guidlines Concerning Thesis Preparation publishedby the Faculty of Graduate Studies and Research:

> " While the inclusion of manuscripts co-authored by the Candidate and others is not prohibited by McGill, the Candidate is warned to make an explicit statement on who contributed to such work and to what extent, and Supervisors and others will have to bear witness to the accuracy of such claims before the Oral Committee. It should also be noted that the task of the External Examiner is made much more difficult in such cases, and it is in the Candidate's interest to make authorship responsibilities perfectly clear. "

All three papers included in this thesis were co-authored by the candidate and his supervisor Dr. A.F. MacKenzie. The candidate has been fully responsible for both conducting the origional studies and for preparing the three manuscripts. Assistance was given by Dr. A.F. MacKenzie through general guidance and editorial comments during the preparation of the manuscripts.

ACKNOWLEDGEMENTS

Financial support from the Natural Sciences and Engineering Research Council of Canada for this study is greatefully acknoledged.

My great appreciation should be first directed to Professor A.F. MacKenzie, under his keen guidance and his consistent support, the present study was done and this dissertation was prepared; to Professors W. Hendershort and I. O'Halloran, for their critical discussion and valuable suggestions throughout the study, and to Dr. R.E. Karamanos, formerly Professor of Soil Science at Macdonald College (now at ESSO Ltd., Lethbridge, Alberta), for his interest in this study.

I am also grateful to Dr. G. Mehuys, Professor and Chairman, to Dr. R. Titman, Professor and former Chairman, to Dr. D. Bird Professor of Renewable Resources, to Dr. J. Fyles, Professor of Forestry, to Dr. D. Smith, Professor of Plant Science, to Dr. T. Moore, Professor of Geography, to Dr. W. Marshall, Professor of Agricultural Chemistry and Food Science, and to Dr. R. Knowles, Professor of Microbiology, to Dr. R.R. Simard at Research Station, Agriculture Canada, Ste-Foy, Quebec, and to Dr. J.E. McFarlane, Professor and Chairman of Department of Entomology for their encouragement, interest and helpful discussion.

Special thanks are given to Dr. T. Bates, Professor of Soil Science, University of Guelph, Guelph, Ontario, for his critical review of the thesis.

I wish to express my great appreciation to Eddy St.George, Peter Kirby and Khosro Mousavi for their assistance in various forms, to the community of the Department of Renewable Resources for creating a warm

climate in which the study was carried out.

I dedicate this work to my wife, Zhijian for her understanding, patience in daily life, self-control and love, in addition to her own heavy studies.

CONTRIBUTIONS TO KNOWLEDGE

The studies presented in this thesis clarified the mechanisms involved in orthophosphate (OP), pyrophosphate (PP) and Zn interactions, and quantified effects of sorbed P on cation exchange capacity (CEC), Zn sorption and desorption, and Zn fractions in soils. Major contributions to knowledge are presented below:

1. Autoclaving changed soil CEC and reduced OP sorption due to conversion of organic-Fe and Al components to materials not extractable with dithionite-citrate.
2. Both PP and OP increased the CEC of autoclaved soils as did OP in non-autoclaved soils, CEC was increased by 0.52 and 1.24 mmole(+) mmole^{-1} sorbed P as OP or PP.
3. In terms of per atom of sorbed P, CEC was increased more with OP than with PP, implying PP sorption with more than two sorption bonds (valence) per molecule PP to soil surfaces. At the same rate of P addition (mmole P kg^{-1} soil), PP resulted in a greater increase in CEC than did OP due to more P sorption as PP than as OP. Greater P sorption with PP was attributed to a greater number of sorption bonds per molecule of PP compared with OP.
4. The sequestering effect of PP on Zn was not significant. Increased Zn sorption by OP or by PP was not due to increased CEC but due to enhanced specific Zn sorption through Zn-P-soil complexes, with PP being more effective than OP, especially in coarser textured soils. Sorbed P as PP had more active linkages, favoring formation of Zn-P complex, compared to OP.

5. The interactions between OP and Zn in non-autoclaved soils or PP and Zn in autoclaved soils occurred mainly in association with Fe or Al components as indicated by increased or decreased correlations between Zn (or P) parameters (sorption, desorption, and fractions) and Fe or Al fractions, suggesting that P application is most likely to induce crop Zn deficiency in soils rich in Fe or Al materials.

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INTRODUCTION

Crop Zn deficiencies have been reported frequently following the application of orthophosphate (OP) fertilizer (Boawn and Brown, 1968; Loneragan et al., 1979; Christensen and Jackson, 1981; Singh et al., 1988). The OP-Zn interaction is believed to appear as two aspects: (i) P-Zn interactions in soils, and (ii) P-Zn interactions in plants. Available evidence has indicated that P-Zn interaction in soil includes a series of hypothetical mechanisms: (1) an increased surface negative charge of soil particle after P sorption, therefore enhancing Zn-ion coulombic sorptions (Saeed and Fox, 1979; Laverdiere, 1982; Barrow, 1987); (2) a precipitate of hopeite ($Zn_3(PO_4)_2.H_2O$) and other complexes between Zn and other soil components (Lindsay, 1979; Pulford, 1986); (3) an imposed pH effect on localized soil zones by added P, influencing Zn solubility (Barrow, 1987; Shuman, 1988); (4) a "bridge" effect of sorbed P increasing Zn fixation by soil particles (Stanton and Burger, 1970a; Bolland et al., 1977); and (5) newly created sorption sites by sorbed P, increasing specific Zn sorption in soils. Information on these mechanisms is often fragmentary and insufficient to explain P-induced Zn deficiencies in crops.

In contrast to OP, pyrophosphate (PP) has been shown to increase Zn uptake by crops in early stages (Singh and Dartiques, 1970; Rehm et al., 1980), perhaps PP sequestering Zn both directly (Slack et al., 1965; Bar-Yosef and Asher, 1983) and indirectly (Mortvedt and Osborn, 1977) thus keeping Zn in solution. Such an effect would be short-lived to the extent that PP hydrolyzes into OP in soils (Dick and Tabatabai, 1986).

In most cases, however, negligible sequestering of Zn by PP has been observed following PP fertilization (Lehr et al., 1967; Schield et al., 1978). This may have been due to (1) PP concentration being too low (the sequestering requires a threshold PP concentration) (Bar-Yosef and Asher, 1983); (2) PP sorption increasing surface negative charge thus increasing Zn coulumbic attraction, as proposed for OP (Saeed and Fox, 1979); (3) PP increasing solubility of Fe and Al oxides (McKeague, 1967; Sheldrick, 1984), and precipitation of Fe- or Al-Zn (Pulford, 1986); and (4) PP increasing specific Zn sorption sites. Therefore it is important to determine effects of added PP on Zn solubility, since understanding of the PP-Zn interaction in soils results in improvement in fertilization techniques and subsequent crop production.

Both OP and PP may have an impact on increasing Zn physico- and chemisorption. Verifying the significance of the mechanisms involved in the OP- or PP-Zn interaction in soils and comparing the OP-Zn and PP-Zn interactions require comparable conditions. It is speculated that both OP and PP sorption would result in increases in coulombic Zn sorption through increased CEC, and in specific Zn sorption through Zn sorption sites newly created by sorbed P. The existance of such a coulombic effect could be verified by testing whether the amount of exchangeable Zn would be increased, and the specific Zn sorption by testing whether the amount of Zn associated with Fe and Al components and the difference between sorbed Zn and exchangeable Zn would be increased. The relative effect of OP and PP could be compared using autoclaved soils in order to minimize PP hydrolysis (Tabatabai and Dick, 1979).

As a result of the above considerations, the objectives of this study were developed as follows:

1. to compare effects of added PP and OP on CEC of soils.
2. to compare effects of sorbed OP and PP on Zn reactions in soils.
3. to evaluate possible mechanisms of OP or PP interactions with Zn.

CHAPTER I

LITERATURE REVIEW

Phosphorus is a macronutrient required for crop production. Application of P as orthophosphate (OP) to soils, however, has been reported to induce Zn deficiency in plants (Loneragan et al., 1979; Singh et al. 1988). Such an effect may be attributed to OP-Zn interactions in soils and OP-Zn interactions in plants, but results from various studies are conflicting (Saeed and Fox, 1979; Barrow, 1987; Shuman, 1988; Singh et al., 1988). Pyrophosphate (PP) as a P fertilizer has increased in popularity due to its high P content, low cost in transportation and ability to chelate metals. The higher complex constant of $P_2O_7^{4-}$ with Zn^{2+} than with other dominant cations (Wolhcff and Overbeek, 1959) has promoted studies on using PP to keep Zn in solution, and increasing Zn uptake by crops. The conclusion that PP fertilizer may eventually increase (Singh and Dartiques, 1970; Rehm et al., 1980) or have no effect on crop Zn uptake (Lehr et al., 1967; Adriano and Murphy, 1970) indicates that the mechanisms involved in PP-Zn interaction in soils and in plants are complicated. A better understanding of the mechanisms controlling OP, PP, and Zn reactions and interactions in soil is an essential preliminary stage to studying P-Zn interactions in plants.

Mechanisms of Orthophosphate Reaction in Soils

Phosphate in the soil is a complex system of solid and solution forms, which vary in their properties and reactions. Among the forms, orthophosphate (OP) is the most favored form for plant use (Sutton and Larsen 1964; Sutton et al. 1966). Orthophosphate may change in the sequence of H_3PO_4 ---> $H_2PO_4^-$ ---> $HPO_4^=$ ---> PO_4^{3-} as pH increases, or the reverse direction as pH decreases. In the pH range of 5.0 to 8.0,

$H_2PO_4^-$ and HPO_4^{2-} are the main P species in solution. Crystal studies showed that PO_4^{3-} ion contains a double pi bond which is equally distributed over all four oxygen linkages as a result of sp atomic orbital hybridization and resonance of the P-O bonds (Corbridge, 1974; 1985).

Of the OP reactions with soils, sorption on soil materials is the predominant phenomenon at low to medium concentrations. This includes specific and nonspecific sorption, diffusion and precipitation into or on the sorbent (Hingston et al., 1967; Rajan and Fox, 1975; Bohn et al., 1979; Cabrera et al., 1981; Barrow, 1983a; 1983b; Willett et al., 1988).

There are at least three types of sorption sites on or in the sorbents postulated by Muljadi et al. (1966a, 1966b, 1966c). The first two types are located on the sorbent surface, while the third type results from diffusion into amorphous regions of the crystal surface (Barrow, 1983a; 1983b; Willett et al., 1988). Different sorbents, i.e., clay minerals and oxide materials, behaved essentially in the same manner and differed only in the number of sorption sites of types I and II. Functional groups (S-OH) or sorption sites increased to a limit with decreases in pH, and the shape of the sorption isotherms remained essentially the same. This is consistent with two stages of P fixation: a rapid initial reaction at sites of types I and II, followed by a relatively slow reaction at site III (Barrow, 1983a; 1983b; Willett et al., 1988).

The initial reaction has been attributed to a sorption of OP through the replacement of OH^- ions, H_2O or other anions on the surface of the soil particles (Hingston et al., 1967; Kuo and Lotse, 1972; Rajan and Fox, 1975; Clark and McBride, 1984; Rao and Sridharan 1984), which is believed to occur in the inner electrical double layer, i.e., Stern layer or Inner Helmholtz Plane (Barrow and Bowden, 1987). Chemisorbed ions are potential determining ions or at least alter the surface potential (Bolan and Barrow, 1984). Orthophosphate P may form a binuclear surface complex with Fe or Al oxides within a rather broad range of P concentrations (Parfitt, 1978; Martin and Smart, 1987).

Nonspecific sorption is generally a coulombic attraction between an anion or cation and a positive or negative charged site on the $AlOOH_2$ or $FeOH_2$ groups of soil materials (Hingston et al., 1967, Greenland, 1971; Everett, 1972) occurring just outside the Stern layer.

The conformity of sorption data to the diffusion model of Barrow (1983b) suggests that the increase in OP sorption with time is induced by a redistribution of sorbed OP into the interior of layer minerals or amorphorus materials by a solid-state diffusion process (Holford and Mattinly, 1975; Ryden et al., 1977; Cabrera et al., 1981; Imai et al., 1981; Bolan et al., 1985). The slow reaction continues by a gradual increase in crystal size of precipitated Fe and Al phosphates, with the metal ions being contributed from the gradual breakdown of clay minerals and hydrous oxides (Haseman et al., 1950; Low and Black, 1950). Recently, Willett et al. (1988) showed that the slow reaction was attributed to the migration and sorption of P ions into/on surface sorption sites of decreasing accessability within aggregated particles of ferrihydrite.

At high rates (>1.0 M) of OP addition, a mechanism of reaction may include OP displacement of silicates in silicate minerals (Rajan and Fox, 1975), or destruction of mineral structures and release of Al and

Fe ions, which form precipitates with P (Low and Black, 1950; Rajan and Fox, 1975). At low pH, the precipitates are mainly Fe-P and Al-P, while at high pH or in calcareous soils, Ca-P is dominant (Savant and Racz, 1973; Lindsay, 1979).

Mechanisms of Pyrophosphate Reactions in Soils

Polyphosphate fertilizers containing predominantly pyrophosphate (PP) have become increasingly important in crop production. Pyrophosphate changes in solution in the sequence of $H_4P_2O_7$ --> $H_3P_2O_7^-$ --> $H_2P_2O_7^=$ --> $HP_2O_7^{3-}$ --> $P_2O_7^{4-}$ as pH increases and in the opposite direction as pH decreases. In a pH range of 5.0 to 8.0, the main species are $H_2P_2O_7^{2-}$ and $HP_2O_7^{3-}$. The reactions of added PP in the soil include sequestering (Slack et al., 1965; Bar-Yosef and Asher, 1983), sorption (Mnkeni and MacKenzie, 1985), hydrolysis (Dick and Tabatabai, 1986), precipitation (Savant and Racz, 1973; Khasawneh et al., 1974; Subbarao and Ellis, Jr., 1975) and dissolution of organic matter (Mortvedt and Osborn, 1977).

Pyrophosphate can complex cations, such as Al, Fe and Zn ions, and solubilize soil organic matter which fixes cations, exposing Fe and Al sesquioxides for P sorption (Mnkeni and MacKenzie, 1985; Stevenson, 1986). The complex constant of $P_2O_7^{4-}$ with Zn^{2+} (10^8) is generally greater than for other dominant cations (Wolhoff and Overbeek, 1959) indicating that $P_2O_7^{4-}$ may keep Zn^{2+} in solution, and this has promoted studies on the effect of PP-Zn interactions on Zn solubility in solutions (Mortvedt and Osborn, 1977; Bar-Yosef and Asher, 1983) and on crop Zn nutrition (Singh and Dartiques, 1970; Rehm et al., 1980). Addition of small amounts of PP has resulted in decreases in OP sorption and in NH_3 volatilization (El-Zahaby and Chien, 1982; El-Zahaby et al., 1982).

In addition to formation of complexes, PP in soils hydrolyzes to OP. The availability of PP for plant use mainly depends on its hydrolysis to OP, although evidence has been obtained that plants can utilize P as PP (Sutton and Larsen, 1964). Hydrolysis of PP is basically a biological process and microbiological or enzymatic activity is generally recognized as the most important factor in PP hydrolysis (Sutton et al., 1966; Gilliam and Sample, 1968; Hashimoto et al., 1969; Subbarao et al., 1977; Dick and Tabatabai, 1986). Hydrolysis of PP appears to be a first-order reaction (Blanchar and Hossner, 1969a; 1969b, Hossner and Phillips, 1971; Dick and Tabatabai, 1978) and in some cases zero-order (Subbarao et al., 1977) with a half-life from a few hours to about 100 days, depending on experimental conditions (Gilliam and Sample, 1968; Blanchar and Hossner, 1969a; 1969b; Hossner and Phillips, 1971; Racz and Savant, 1972; Juo and Maduakor, 1973; Parent and MacKenzie, 1985; Dick and Tabatabai, 1986). Factors affecting the rate of PP hydrolysis were, in decreasing order of importance, temperature, pH, enzymes, presence of colloids, complexing cations, P concentration, and ionic environment in the solution (van Wazer, 1958). Attempts to determine the individual contribution of one or more of these factors have met with only partial success (Sutton et al., 1966; Gilliam and Sample, 1968; Blanchar and Hossner, 1969a; 1969b; Hashimoto et al., 1969; Savant and Racz, 1972a; 1972b; Al-Kanani, 1985). Neutral pH, high moisture contents, low OP concentrations, moderately high temperatures, and media with low P sorption capacities are generally favoured for high pyrophosphatase activities (Blanchar and Hossner, 1969a; 1969b; Hossner and Phillips, 1971; Racz and Savant, 1972; Savant and Racz, 1972b). Cations, such as Mg^{2+}, Zn^{2+}, Fe^{2+}, may have an activation effect on pyrophosphatases (Searle and Hughes, 1977). Chemical catalysis alone will promote the hydrolysis but probably not at a rate adequate for the needs of the crop. The rate of PP hydrolysis in the soil could be minimized by eliminating microbial and enzymatical activities through autoclaving or adding toluene to soil (Douglas et al., 1976; Tabatabai and Dick, 1979).

Pyrophosphate sorption is another important PP reaction in the soil. Several studies have shown that sorption capacities for PP were higher than for OP (Sutton and Larsen, 1964; Blanchar and Hossner, 1969a; 1969b; Al-kanani, 1985; Mnkeni and MacKenzie, 1985), and the difference was accentuated at lower pH values (Blanchar and Hossner, 1969b). Pyrophosphate sorption was stronger (Hashimoto et al., 1969) but less rapid (Philen and Lehr, 1967) than OP sorption, and yielded markedly different reaction products (Savant and Racz, 1973; Lindsay, 1979). In contrast, Sutton and Larsen (1964) showed that the sorption of OP was stronger than PP. There is lack of agreement in regard to the energy of sorption of PP and OP anions by soils. Sutton and Larsen (1964) reported a lower bonding energy for PP as compared to OP but Hashimoto et al. (1969) reported the opposite.

Studies on PP sorption mechanisms are lacking (Parfitt, 1978). A binuclear complex of PP ions with two to four phosphate oxygens in coordination with two ferric or aluminum ions on the mineral surfaces, could be hypothezied. However, PP ions are larger than OP ions, and one could consider linkage with sorbed cations, such as Ca^{2+} or Mg^{2+}, rather than replacement of hydroxyl groups by PP. Evidence has shown that clays saturated with divalent ions sorbed more P than clays saturated with monovalent ions (Pissaides et al., 1968). Polyphosphate sorption was curvilinearly related to extractable Fe and Al contents, in contrast to linear relationships obtained with OP sorption (Mnkeni, 1983). Other studies have shown that the PP sorption was partly the replacement or dissolution of organic matter by PP (Mortvedt and Osborn, 1977; Mnkeni and MacKenzie, 1985). Thus adding organic materials resulted in decreased PP sorption (Mnkeni and MacKenzie, 1985).

Mechanisms of Zinc Reactions in Soils

Zinc in the soil solution could appear as Zn^{2+}, $ZnOH^+$, and $Zn(OH)_2$ (Lindsay, 1979). The proportion of hydroxyl Zn increases as pH increases. The main species of Zn in soil solution with a pH range of 5.0 to 8.0 are Zn^{2+} and $ZnOH^+$. Other Zn species in soils include the oxides, carbonates, phosphates and silicates (Lindsay, 1979; Mikkelsen and Kuo, 1977). The main reaction of added Zn in the soil is a sorption-desorption ($pH < 7.0$) or precipitation-dissolution ($pH > 7.0$) process (Brummer et al., 1983).

Clay minerals (Bingham et al., 1964; Reddy and Perkins, 1974), sesquioxides (Jenne, 1968; Stanton and Burger 1970a; 1970b), carbonates (Udo et al., 1970), and soil organic matter (Tan et al., 1971) have been suggested as major materials accommodating added Zn in soils. Formation of Zn silicates may control Zn concentration in solution if natural complexing agents are absent (Brummer et al., 1983), formation of Fe-Zn and P-Zn precipitates has also been suggested (Lindsay, 1979; Pulford, 1986). Formation of other Zn compounds is unlikely in most soils because large amounts of Zn are required to ensure saturation of sorption sites before precipitation occurrs, except in calcareous soils with high pH values. Ion exchange between Zn^{2+} and other cations, such K^+, Ca^{2+} and Mg^{2+}, is also possible (Emmerich et al., 1982; Neilsen et al., 1986; Singh et al., 1988).

Two types of sorption, non-specific or reversible and specific or irreversible, occurred on the surface of soil particles (Kalbasi et al., 1978; Kinniburgh, 1983). Zinc is specifically sorbed through replacement of H^+ ions on sorbent surfaces. The ratio of mole protons released per mole Zn sorbed varies between 1 and 3.2, and the net release of H^+ by Zn^{2+} sorption was shown to be independent of pH (Benjamin and Leckie, 1981; Kinniburgh, 1983; Kinniburgh et al., 1983; Kuo, 1986; Gupta et al., 1987). The oxides of Fe and Al sorb Zn by two different mechanisms, one involving OH^- and the other HPO_4^- (Stanton and Burger, 1967; 1970a). Both are specific for Zn to the extent that Ca^{++}, Mg^{++}, K^+ and NH_4^+ do not interfere. Quirk and Posner (1975) suggested an olation bridge and ring structure as a mechanism of Zn^{2+} sorption on goethite surfaces. Bingham et al. (1964) and Barrow (1986b) argued that the species associated with Zn sorption is $ZnOH^+$, with an initial rapid sorption of $ZnOH^+$ ions onto heterogenous charged surfaces, followed by a diffusive penetration. Wegmuller (1987) concluded that uncharged Zn-aquo-hydroxide was the sorbing Zn species and reacted at neutral to alkaline pH. In other studies, Zn^{2+} was shown to be the principle species for Zn sorption (Kalbasi et al., 1978; Singh and Abrol, 1985).

Evidence (Barrow, 1986a; Hayes and Leckie, 1987) indicated that part of the strongly bound Zn enters into the crystal lattice of layer minerals. Such strongly bound Zn may reduce the exchange capacity, suggesting that the sorption is taking place inside of the Stern plane. Equilibrium was not readily attained but tended to approach a slow steady state after several days (Barrow, 1986a).

Sorption Isotherms

Models describing sorption behaviour on soil materials have been developed, and may be categorized into five groups: (1) equilibrium models, including Linear, Gunary, Temkin, Freundlich, Langmuir, two surface Langmuir, and competitive Langmuir isotherms; (2) kinetic models, including reversible linear, reversible nonlinear, kinetic product linear, mass transfer, Elovich, Fava, Eyring and two-site kinetic models with theoretical bases of these models detailed by Travis and Etnier (1981) and Ratkowsky (1986); (3) constant capacitance models, including Stern (Barrow et al., 1980; Bowden et al., 1980; Bolan and Barrow, 1984), mechanistic (Barrow, 1983b) and chemical models (Goldberg and Sposito, 1984; Goldberg, 1985), developed on the bases of both charge and chemical changes occurring in the process of ion sorption reactions in the system (Bolan and Barrow, 1984; Goldberg and Sposito, 1984); (4) multi-factor kinetic models (Novak and Petschauer, 1979; Lin et al., 1983a; 1983b), which could account for several factors involved in the sorption process and have been introduced to define P sorption on minerals and in acidic soils by Lin et al. (1983b); (5) objective model (Sposito, 1984; Barrow and Bowden, 1987), in which the P ions are allocated to four planes.

Despite the existance of various sorption isotherms, the Freundlich and the Langmuir equations remain the preferred choice for describing anion or cation sorption behaviour in soil systems (Shuman, 1977; Sidle et al., 1977; El-Zahaby and Chien, 1982; Ratkowsky, 1986). The Langmuir equation is represented as:

$$C/S = (1/kb) + C/b \qquad (1)$$

and the Freundlich equation is experessed as:

$$S = K\ C^N \qquad (2)$$

or

$$\ln S = \ln K + N \ln C \qquad (3)$$

where, C is the solute concentration at equilibrium, S is the solute sorbed, b, k, K and N are coefficients. The Freundlich isotherm may be obtained from the Langmuir theory of monolayer sorption by assuming that the energy of sorption is a logarithmic function of the surface coverage (Travis and Etnier, 1981). Sorption of P by the soil was described better by the Freundlich or modified Freundlich than by the Langmuir equation (Barrow, 1978; Sibbesen, 1981; Ratkowsky, 1986), while in other studies, P sorption on soil materials showed a closer agreement with the Langmuir isotherm than with other sorption isotherms (Cole et al., 1953; Olsen and Watanabe, 1957; Larson, 1967; El-Zahaby and Chien, 1982). Zinc sorption was described by Langmuir sorption isotherms (Udo et al., 1970; Shuman, 1975; 1976; 1977) or more successfully, by the modified Langmuir equation (Boyd et al., 1947; Griffin and Au, 1977; Sposito, 1979), which allowed for ion exchange reactions (Harter and Baker, 1977), and pH dependence (Bar-Yosef, 1979), while Sidle et al. (1977) used Freundlich sorption isotherms to characterize Zn sorption in a forest soil.

The importance of finding a best-fit sorption isotherm is (1) to simulate solute convective-dispersive transport in the soil under specific conditions, and (2) to help in understanding the mechanisms involved in the physical and chemical transformations of the solute. Given the complexity of solute-water-soil systems, various sorption isotherms provide reasonably good interpolation of data. A plot of C/S against C for the Langmuir isotherms and lnS against lnC for the Freundlich isotherms should give a straight line. However, non-linear isotherms are often obtained (Olsen and Watanable, 1957; Larsen et al., 1965; Shuman, 1975). One explanation is that sorption includes several stages, or different sorption sites and the energy of solute sorption is not constant. These sites are associated with a high-energy chemisorption, including diffusion sorption, chemisorption, precipitation and a low-energy (physical) sorption (Bache, 1964; Muljida et al., 1966b; Kuo and Lotse, 1972; Shuman, 1975; Ryden et al., 1977; Willett et al., 1988). The coefficients in the sorption isotherms have been shown to relate to the nature of the sorbent, and were energy associated, e.g., the sorption maximum calculated from the Langmuir isotherms was closely correlated with CEC and clay content (Shuman, 1975), surface area (Borggaard, 1983a), carbonate (Udo et al., 1970) and organic matter contents (Shuman, 1975; Bar-Yosef, 1979). The coefficients of N in the Freundlich and k in the Langmuir isotherm are considered to be bonding coefficients (John, 1972; Shuman, 1975), and thus can be used to describe sorption behaviour.

Factors Affecting Phosphate or Zinc Sorption in Soils

Factors affecting P and Zn sorption are mainly contents of Al and Fe hydrous oxides (Parfitt et al., 1975; Shuman, 1976; Borggaard, 1983a; 1983b; Laverdiere and Karam, 1984; Mnkeni and MacKenzie, 1985), types of sorbent (Karim and Adams, 1984; Ainsworth et al., 1985), and pH (Bar-Yosef, 1979; Clark and McBride, 1984) in addition to other factors such as organic matter, ionic strength, time, temperature, moisture content of the system (Sharpley and Ahuja, 1982; Sheppard and Racz, 1984; Bolan et al., 1985; Mnkeni and MacKenzie, 1985), and microbial and enzymatic activities (Rao, 1979; Tinker and Gildon, 1983).

Sorbent Materials

The sorption ability of iron oxides depends on their crystallinity. Noncrystalline forms and forms with short range order (amorphous) sorbed more OP per unit weight than crystalline forms or layer silicates (Gastuche et al., 1963; Bache, 1964; McLaughlin et al., 1981), but no correlation between P sorption and noncrystalline oxide was shown, indicating that an initial precipitate of P and the noncrystalline oxide occurred. Crystalline oxides were correlated with OP sorption in various Oxisols (Jones, 1981; Karim and Adams, 1984).

Differences in the extent of P sorption appeared to be primarily related to the number of functional (S-OH) groups present at the solid-solution interface or surface area (Ainsworth et al., 1985). However, various synthetic iron oxides sorbed nearly equal amounts of OP when expressed per unit of surface area (McLaughlin et al., 1981; Borggaard, 1983a). Allophanic materials sorbed appreciably more OP than other Fe, Al and kaolinite materials (McLaughlin et al., 1981; Moody and Radciliffe, 1986), and together they accounted for the predominnat P-sorbing sites.

Solubility of P and Zn has been related to content of soil Fe and Al oxides (Shuman, 1976; Lindsay, 1979; Borggaard, 1983a; 1983b; Karim and Adams, 1984; Laverdiere and Karam, 1984; Pulford, 1986). The P and Zn concentrations may be controlled by the Al and Fe activities of the solution. Thus high activities of Al and Fe have resulted in less soluble P (Lindsay, 1979) and Zn (Shuman, 1976; Kuo, 1986; Pulford, 1986). The formation of Fe- or Al-P in acid soils, and Ca-P in alkaline soils is governed by the solubility product principles, the common ion principle, and the salt effect principle. Thus removal of the free Fe oxide from the soil colloids reduced the magnitude of P sorption (Borggaard, 1983b), and Zn sorption (Shuman, 1976). Both P and Zn ions may diffuse into or be sorbed at the less accessible sorption sites of the amorphous Al and Fe materials, resulting in a slow reaction (Ellis and Troug 1955; Barrow, 1986a; Willett et al., 1988).

Soil pH

The direct effects of pH include increases in pH which result in a more negative surface and less positive PP and Zn ions in solution. Indirect effects include dissolution or crystallization of Fe or Al materials.

Hydroxyl groups in solution compete with OP for the sorption sites. Thus increases in pH result in less OP sorption (Imai et al., 1981; Asher and Bar-Yosef, 1982; Bolan and Barrow, 1984; Iniguez and Val, 1984). However, Stanton and Burger (1970b) showed that P sorption increased as the pH increased, up to a value of 6.25, with further increases in pH resulting in decreased sorption.

Zinc sorption is highly pH-dependent (Kinniburgh and Jackson, 1982; Tiller et al., 1984; Gupta et al., 1987). This strong pH-dependence has been interpreted in terms of several mechanisms: the preferential sorption of hydrolyzed cation $ZnOH^+$, the formation of surface-$Zn(OH)^+$ species, or the exchange of Zn^{2+} for surface bound protons (Morel et al., 1981; Schendler, 1981; Barrow, 1986b), and the attraction between a more negative surface and the cation. Total and specifically sorbed Zn increased with pH increases. The non-specifically bound Zn also generally increased somewhat with pH but less than other forms, up to a maximum at pH 5.6, then decreased (Tiller et al., 1984). At high pH, precipitation controls Zn solubility (Lindsay, 1979).

Organic Matter

More OP was sorbed when the soil contained less organic matter (Imai et al., 1981). Loosely bound organic matter is progressively displaced by reactive OP ions. At pH above 7, the effect is less pronounced. In the presence of organic anions, P sorption by soils is reduced (Appelt et al., 1975; Lopez-Hernandez et al., 1986).

Organic acids were capable of reducing the amount of P (PP and OP) sorbed by minerals probably due to competition between OP or PP and organic anions for sorption sites (Nagarajah et al., 1970; Lopez-Hernandez and Burnham, 1974; Holford and Mattingly, 1975; Mnkeni and MacKenzie, 1985). On other hand, organic matter may retain P in association with cations such as Fe^{3+}, Al^{3+}, and Ca^{2+} (Wild, 1950). Furthermore, organic acids could perturb the crystallization of Al and Fe oxides (Thomas, 1975; Wallingford et al., 1975; Ng Kee Kwong and Huang, 1978), reduce the diffusion coefficient (Warnecke and Barber, 1973) or form complexes in association with soil particles (Hodgson et al., 1966) thus directly or indirectly affecting P and Zn solubility in soils. Other effects include organic matter buffering of soil pH

(Magdoff and Bartlett, 1985; Curtin et al., 1987), and enhancing or depressing microbial activities (Frankenberger and Dick, 1983), which indirectly influence P or Zn solubility. The combined effect of organic matter on Zn or P sorption depends on the balance between these reactions.

Salt Concentration or Ionic Strength

Increasing the concentration of background electrolyte increases OP retention at high pH (Helyar et al., 1976; Robarge and Corey, 1979), but at low pH, increasing electrolyte concentration decreased OP sorption (Barrow et al., 1980).

Zn sorption has been reported to be greater in chloride than in nitrate solutions (Forbes et al., 1976; Padmanabham, 1983), suggesting that the formation of Zn-Cl complex ions favors specific sorption. Elrashid and O'Connor (1982) found no difference in Zn^{2+} sorption on a sandy loam soil using Cl^-, NO_3^-, and $SO_4^=$ at concentrations ranging from 0.005 to 0.1 M at pH 7.6. According to Shuman (1986), ionic strength and anions had no influence on the shape of the isotherms but the higher the ionic strength the less Zn^{2+} is sorbed. Bohn et al., (1979) explained that dilution of equilibrium solutions favored retention of more highly charged cations, and Barrow and Ellis (1986) indicated that Zn sorption was decreased by high concentration of salt partly due to effects of salt in decreasing soil solution pH. Increasing the salt concentration would reduce the negative potentials thus decreasing Zn sorption. Increased Zn sorption in the $SO_4^=$ system could be due to changes in the surface potential after $SO_4^=$ sorption (Benjamin and Leckie, 1982). On the other hand, complexed Zn, such as $ZnSO_4$ or $ZnCl^+$

may be favored for specific sorption because of the reduction in hydration and in the electrical charge of the Zn^{2+} (Padmanaham, 1983). As expected, Zn desorption in calcium solutions was greater than in sodium solutions (Barrow, 1986) due to replacement of sorbed Zn by Ca^{2+}.

In summary, ionic strength influences: (1) anion competition with P ions for sorption sites; (2) surface potentials and thickness of the diffuse layer; (3) anion sorption which in turn affects surface potential; (4) solution complexes of Zn with anions which enhance Zn sorption; (5) surface complexes of Zn with anions which reduce Zn desorption; (6) background cations which displace H^+ from the surface, decreasing solution pH, and (7) the ion exchange process between the solute and sorbate on the sorbent.

Temperature

The rates of both OP sorption and desorption are increased with increases in temperature (Barrow, 1979; Chien et al., 1982; Barrow, 1986a). There was a more than threefold increase in the rate of change of P for each 10°C increase in temperature (Barrow, 1974).

The effect of temperature on P (PP and OP) and on Zn sorption was attributed to increased sorption sites resulting from high temperature. Under such conditions, both the functional groups on the surface and the solutes in solution are in a high energy state, increasing reactions rates. Kuo and Mikkelsen (1979) showed that increasing temperature increased the rate of Zn reaction with soil, probably due to the increases in the concentration of $ZnOH^+$ ions (Barrow, 1986a).

Moisture Levels

With moisture contents greater than field capacity, sorption should be increased due to more freedom of movement of solutes in the soil-solution system, with more frequent contact between solutes and sorption sites. The extent of P movement was influenced more by initial soil moisture content than by the source of P (Khasawneh et al., 1974). However, high solution:soil ratio decreased and low ratio increased P sorption in the range of 5:1 to 40:1 (Hope and Syers, 1976). The kinetic control of solution:soil ratio on ion sorption may be interpreted in terms of the number of ion sorbing sites and initial solute concentrations on the rates of ion sorption by soils. The sorptive capacity of a solid for a solute tends to increase as the fluid phase concentration of the solute increases. Yet, air-drying was shown to increase OP sorption capacity of some soils (Barrow and Shaw, 1980; Haynes and Swift, 1985). Other effects include moisture contents affecting redox conditions, which influence Fe and Mn solubilities and in turn, control Zn solubility (Sajwan and Lindsay, 1986).

Reaction Time

Sorption equilibrium is not readily attained but tends to approach a slow steady state after several days (Tiller and Hodgson, 1962; Kuo and Mikkelsen, 1979; Barrow, 1986a). Zinc continued to react with soils for up to 30 h, the change in concentration was proportional to a fractional power of time (Barrow, 1986a). Non-specific sorption was more rapid than specific sorption. The highest values of non-specific sorbed Zn were recorded at 2 h, and thereafter either changed little or decreased somewhat because of the transfer to specifically bound forms.

Specific sorption was much more rapid during the first 2 or 3 days than later, especially at high pH values (Tiller et al., 1984). Thus as time goes on, the reactions between solute ions and sorbent change in the sequence of rapid non-specific, then specific, and finally, penetration or slow sorption into/in the interior surface of amorphous and crystalline materials.

Phosphate and Zinc Interactions in Soils

Most studies of the effect of P on solubility or extractability of Zn in soil have found either negligible or conflicting results, even when Zn deficiencies in crop have been worsened by P additions (Adams, 1980; Adams et al., 1982; Olsen, 1972; Norvell et al., 1987; Shang and Bates, 1987). Loneragan et al. (1979) suggested that one of the reasons for P-induced Zn deficiency in plants could be P-enhanced Zn sorption by sesquioxides. A decrease in available Zn occurred when P was applied to acid soils (Badanur and Rao, 1973). Murphy et al. (1981) and Shang and Bates (1987) reported that the availability of Zn was low in calcareous soils or in soils of high pH and that added P enhanced Zn deficiencies more easily under high pH or alkaline conditions (Norvell et al., 1987). Shang and Bates (1987) suggested that Zn soil tests should be adjusted for fertilizer P. Kuo (1986) indicated that no obvious complementary effect of Zn sorption on P sorption, or vice versa, was observed using Fe-oxide, which is consistent with the results of Pasricha et al. (1987) who showed that applying P to the soil did not decrease Zn intensity in the soil solution. According to Al-Showk et al. (1987) and Mandal and Haldar (1980), P addition, regardless of source, had no effect on DTPA-Zn, an index of available Zn in the soil.

However, the sorbed P plays important roles in Zn sorption on soils (Stanton and Burger, 1967; 1970a; 1970b) in addition to those played by organic colloids (Karam et al., 1983) and pH (Kalbasi et al., 1978; Reddy and Perkins, 1974). Several mechanisms are involved in OP-Zn interaction in the soil. (1) A coulombic effect, i.e., P sorption on soil surfaces could change the surface charge towards more negative values (Parfitt et al., 1975; Laverdiere, 1982), thus increasing Zn sorption (Saeed and Fox, 1979; Barrow, 1987). If such increased Zn sorption is due to the coulombic effect, then the amount of exchangeable Zn should be increased and Zn uptake by plants should be enhanced since exchangeable Zn has been proposed as an available form for crop use (LeClaire et al., 1984). (2) A precipitation effect, which included a direct or indirect effect. A direct effect is that $H_2PO_4^-$ and Zn^{2+} form a precipitate of hopeite (Jurinak and Inouye, 1962; Lindsay, 1979), which may not affect Zn availability since this precipitate has relatively high solubility, being adequate for crop uptake (Carroll and Loneragan, 1968). An indirect effect is that P precipitates Ca, Fe and Al components (Kim et al., 1983; Lindsay, 1979; Taylor and Gurney, 1965) or imposes its pH on the localized soil zones (Al-Showk et al., 1987: Barrow, 1987; Shuman, 1988), affecting Fe solubility. Thus Zn solubility would be affected. (3) A bridge effect, where Zn may be sorbed on the surface of oxides of Fe and Al by two mechanisms, one involving OH^- and the other $HPO_4^=$. Stanton and Burger (1970a) and Bolland et al. (1977) stated that Zn is sorbed on phosphated hydrous oxides through the medium of polyvalent bonds which are bonded to both the oxide and Zn^{2+}. Thus, the sorbed P acts as a bridge between soil minerals and Zn, increasing

Zn sorption. This sorbed Zn could be potentially available for plant use. On the other hand, sorbed Zn could also act as a bridge between P and soil materials. Thus Zn sorption should result in increased P sorption. (4) A specific sorption effect, i.e., sorbed P induces Zn specific sorption either through creating new sorption sites or exposing existing sites.

Pyrophosphate has been shown to maintain certain metallic cations in soil solution through sequestration (Rogers and Reynolds, 1949; Wilbanks et al., 1961; Asher and Bar-Yosef, 1982). This fact has led to work verifying the speculation that PP, when applied to soil, sequesters native and applied Zn and thus increases its concentration in soil solution (Gilliam and Sample, 1968; Singh and Dartigues, 1970; Giordano et al., 1971; Bar-Yosef and Asher, 1983). The effectiveness of PP in complexing Zn was dependent on the levels of Ca, Fe, Al, initial PP concentration and pH of the solution in contact with the sorbent. Application of P to a soil resulted in a significant increase in Zn in soil solution, with PP causing more complexing than with OP (Giordano et al., 1971; Hashimoto and Wakefield, 1974; and Mortvedt and Osborn, 1977). The complexing effect of PP is only temporary due to hydrolysis of PP in microbially active soils. Maximum complexing power of PP is expected to be at pH > 9.0, where PP is predominantly $P_2O_7^{4-}$, which forms the most stable complex with Zn^{2+}. The effect of PP on Zn solubility in soils can also be attributed to PP-solubilized organic matter (Mortvedt and Osborn, 1977). Since P sorption as PP is rapid and greater than OP sorption, the degree, however, to which PP sorption in soil leads to decreases in complexing effectiveness of PP for Zn, remains to be investigated. On the other hand, whether the sorbed PP would lead to a shift of the surface charge of the sorbent towards more negative values, increasing CEC, and creating more exchange sites, and thus resulting in increased Zn sorption, remains to be determined.

Zinc Fractions in Soils

The importance of Zn fractionation in soil has two aspects (1) as a reference for soil Zn availability to crops, and (2) as a criterion to investigate Zn sorption mechanisms. Zinc fractions in soil can be partitioned into exchangeable, sorbed, organic, carbonate, sulfide, Mn oxide, amorphous Fe oxide, crystalline Fe oxide and residual forms by using various extractants sequentially (Table 1).

Exchangeable (coulombic attracted) and sorbed (ligand exchange) forms are highly bioavailable, and the organic form is a strongly labile plant-available Zn pool. Other Zn forms, except for residual Zn, represent reservoirs of potentially bioavailable Zn (LeClaire et al., 1984). Studies from California on Holland, Ramona and Helendale soils and from industrial northwestern Indiana on Oakville and Plainfield soils found most of soil Zn in organic and residual forms (Emmerich et al., 1982; Miller and McFee, 1983). Exchangeable and organic forms of Zn increased with decreases in soil pH, but specifically sorbed and Mn-oxide Zn fractions increased with the increases in soil pH for typic Fluvaquents on the Mississippi River alluvium and for soils located in Virginia (Iyengar et al., 1981; Sims and Patrick, 1978). Reports from Ludhiana, India indicated that added Zn was mostly in weakly sorbed and organic fractions in Fathehpur sandy loam soil (Chandi and Takkar, 1982). The soil Zn forms were shown to be affected by environmental conditions (Miller and McFee, 1983), sewage-sludge applications (LeClaire et al., 1984; Emmerich et al., 1982; Sposito et al., 1982), and tillage practices (Shuman and Hargrove, 1985). Little information is available about the effect of added P, especially PP, on native or added Zn distributions.

Singh et al. (1988) failed to show evidence that P-induced Zn deficiency was a result of differences in soil characteristics or water soluble plus exchangeable, organically bound, Mn- and Fe-oxide bound or residual Zn fractions, while Shuman (1988) reported that P additions resulted in a shift of Zn from Mn-oxide and crystalline Fe-oxide fractions to the exchangeable Zn fraction in soils due to an initial lowered pH by added P. Residual Zn was considered most stable, and a shift from other forms to residual forms has been indicated (Emmerich et al. 1982).

A problem in the process of metal fractionation is that extractants are only relatively selective for a specific metal fraction (Tessier et al., 1979). Thus selection of an extractant should be on the basis of (1) if it is effective in extracting the expected fraction, and (2) if it is efficient or plausible under the defined conditions. This is probably why various extractants have been employed in partitioning Zn fractions in different studies (Table 1).

CONCLUSIONS AND HYPOTHESES

The main reaction of OP, PP and Zn in soils is sorption on soil components, especially on Fe or Al oxides. High surface area, low organic matter content, low ionic strength, high temperature, moderate moisture content and longer contact time favor P or Zn sorption, and high pH results in more Zn but less P sorption. Most studies have indicated that sorption can be described best by the Freundlich or the Langmuir isotherms. With sorbed P, it would be expected that there were more available sorption sites on the soil particles as the surface becomes more negative. Thus sorbed P would increase Zn sorption. Whether such increased Zn sorption is attributed to the P-induced coulombic effect, or P-induced specific sorption, or other mechanisms, could be examined by means of Zn sorption-desorption, and fraction distribution in soils. Furthermore, Zn reactions would be affected to a greater extent in the presence of added PP than in the presence of added OP since PP sorption is usually greater than OP at the same rate of P addition.

As a consequence, the objectives of this thesis were:

1. to determine quantitatively the effects of added PP on CEC of soils in comparison with that of OP,
2. to determine the effects of sorbed OP and PP on sorption-desorption and fractions of Zn in soils,
3. to relate P, Zn sorption-descrption and fractions to soil components, and
4. to evaluate mechanisms involved in OP or PP interactions with Zn in soils.

Table 1. Extractants employed in extracting Zn fractions in various studies.

Study		Water soluble	Exchangeable	Specifically sorbed	Organically sorbed	Carbonate bound	Chelate extractable (Complexed)	Sulfide	Mn-oxide bound	Fe+Al oxide bound	Crystalline sesquioxide	Residual
Emmerich et al.,	1982	-	0.5 M KNO_3	H_2O	0.5 M NaOH	0.05 M Na_2-EDTA	-	-	-	-	-	4 M HNO_3
Levesque & Mathur,	1988	H_2O	1 N $CaCl_2$	2.5% HOAc	-	0.1 M HCl	-	4 N HNO_3	-	-	-	-
Maudal & Maudal,	1987	-	1 M NH_4OAc	-	0.05 M $Cu(OAC)_2$	-	0.05 M DTPA +0.1 M TEA	Aq. KCN	-	Aq. $CaCl_2$ +Hydroquione	-	-
Miller and McFee	1983	H_2O	1 N KNO_3	-	1.0 M $Na_4P_2O_7$	0.1 M EDTA	0.2 M $(NH_4)_2C_2O_4$	-	-	0.2 M $(NH_4)_2C_2O_4$	0.3 M NaCl +0.1 M $NaHCO_3$ +0.13 M $Na_2S_2O_4$	-
Neilsen et al.,	1986	-	1 M $MgCl_2$	-	30% H_2O_2	-	-	1 N HNO_3	0.1 M $NH_2OH.HCl$ +0.01 N HNO_3	-	0.27 N Na-Citrate +0.1 N $NaHCO_3$ +0.14 M $Na_2S_2O_4$	HNO_3 +H_2O_2
Shuman & Hargrove	1985	-	1 M $Mg(NO_3)_2$	-	0.7 M NaOCl	-	-	-	-	0.2 M $(NH_4)_2C_2O_4$ +0.2 M $H_2C_2O_4$	-	HF +HNO_3 +HCl
Singh et al	1988	-	0.05 M $CaCl_2$	2.5% HOAc	0.1 M $K_4P_2O_7$	-	-	-	0.1 M NH_2OH HCl	0.2 M $(NH_4)_2C_2O_4$ +0.2 M $H_2C_2O_4$	0.1 M Ascobic acid +0.2 M $(NH_4)_2C_2O_4$ +0.2 M $H_2C_2O_4$	HF +HNO_3 +HCl
Sposito et al	1982	-	0.5 M KNO_3	H_2O	0.5 M NaOH	0.05 M Na_2-EDTA	-	-	0.1 M $NH_2OH.HCl$ +0.01 N HNO_3	0.2 M $(NH_4)_2C_2O_4$ 0.1 M $H_2C_2O_4$	-	HF +HNO_3 +HCl
Sedberry & Reddy	1976	H_2O	1 N NH_4OAc	-	30% H_2O_2	-	0.025 M $Cu(OAc)_2$	-	-	-	-	H_2SO_4 +HF +$HClO_4$
Gupta and Chen	1975	H_2O	1 M NH_4OAc	-	30% H_2O_2 +0.1 M HNO_3	-	-	-	0.1 M $NH_2OH.HCl$ +0.01 M HNO_3	0.2M $H_2C_2O_4$	-	HNO_3 +HF +$HClO_4$
Sims and Patrick	1978	H_2O	1 M NaOAc	-	0.1 M $K_4P_2O_7$	-	-	-	0.1 M $NH_2OH.HCl$ +0.01 M HNO_3	0.2M $H_2C_2O_4$ 0.2M $(NH_4)_2C_2O_4$	-	HNO_3 +HF +$HClO_4$

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CHAPTER II

EFFECTS OF SORBED ORTHOPHOSPHATE ON THE ZINC STATUS OF THREE SOILS OF EASTERN CANADA

INTRODUCTION

Zinc deficiencies in crop production have been noted in Eastern Canada. The interaction of P with Zn and increasing use of P fertilizers suggests that Zn deficiencies may become more widespread. Thus evaluation of the impact of added P on Zn is important for soil management purposes.

Zinc has been shown to be sorbed on the surface of oxides of Fe and Al by two mechanisms, one involving OH^- and the other involving $HPO_4^=$ (Jurinak & Inouye, 1962). Stanton & Burger (1970) and Bolland et al. (1977) argued for a "bridge" effect in which Zn was sorbed on phosphated hydrous oxides through the medium of polyvalent bonds to both the oxide and Zn^{2+}. Increased negative charge or cation exchange capacity (CEC) with sorbed P has been found by a number of workers (Mekaru & Uehara, 1972; Kuo & McNeal, 1984; Gillman & Fox, 1980), and was thought to be responsible for the increases in Zn sorption (Saeed & Fox, 1979). However, Barrow (1987) postulated that Zn and P were sorbed at sites of opposite charge on the surface. Variations in Zn sorption with added P were attributed to a P-induced pH effect (Barrow, 1987; Xie and MacKenzie, 1988). In addition, Xie and MacKenzie (1988) and Neilsen et al. (1986) speculated that P sorption increased specific sorption sites of Zn and that such specifically sorbed zinc was not readily displaced by other cations. The relative importance of P additions on Zn sorption seems to vary with soils of different physical and chemical characteristics.

Information on P-Zn interaction in soils could be obtained from relationships between Zn desorption and soil components at a constant pH. If increased Zn sorption is due to increased negative charges with added P then Zn desorption with added cations would be reversible. If there exists a bridge effect, the amount of desorbed Zn should be proportional to the amount of desorbed P. If, however, added P increases specific sorption sites for Zn there should be reduced Zn desorption with added P. Such an effect could be stronger in soils of high Fe contents than in soils of low Fe contents, since Fe materials may control Zn solubility in soils of high Fe contents (Pulford, 1986).

A further distinction of decreased Zn solubility in soils with added P can be made using Zn partitions. Fractionation of Zn into exchangeable Zn, organic and Fe oxide associated-Zn and residual Zn, or various available forms using different extractants has been attempted (Neilsen et al., 1986; Shang and Bates, 1987; Xie and MacKenzie, 1988). Xie and MacKenzie (1988) discussed pH effects on P-Zn interactions and Zn partitions but did not discuss the effect of soil properties on Zn sorption, Zn desorption and Zn fractions. The impact of added P on such Zn fractions could help to evaluate P-Zn interactions.

Finally, possible Zn-P interaction lies in the precipitation of hopeite. This compound has been considered to be too soluble to explain Zn-P interactions in soils (Lindsay, 1979). However, the possibility of precipitation of hopeite in localized regions of high P concentration may exist.

The present study was designed to determine the effect of soil properties on orthophosphate sorption, of P sorption on CEC, and of soil properties and P sorption on Zn sorption, Zn desorption and Zn fractions, and to evaluate several mechanisms involved in P-Zn interaction in soils.

MATERIALS AND METHODS

Top and subsoil samples were obtained from cultivated Uplands and Dalhousie soil and a pastured St Bernard soil from south-western Quebec, Canada, indicated as UT, US, DT, DS, ST and SS, respectively. Soils were selected to represent those developed on alluvial, marine-lacustrine and glacial till deposits (Table 1). Samples were air dried, ground to <1 mm and analyzed for pH, organic C, CEC, phosphate sorption maxima, clay content, dithionite-citrate extractable Fe and Al (DC-Fe and DC-Al), ammonium-oxalate extractable Fe and Al (AO-Fe and AO-Al), and sodium pyrophosphate extractable Fe and Al (PP-Fe and PP-Al). Crystalline Fe (Fe_{CRY}) was defined as DC-Fe minus AO-Fe, amorphous Fe (Fe_{AM}) as AO-Fe minus PP-Fe, and organic Fe (Fe_{OR}) as PP-Fe. Zero point of net charge (ZPNC) was determined.

Experiment 1. P Sorption Effects on Soil CEC

Six soil samples, 5 P solution levels (0.0, 12.0, 30.0, 60.0, and 90.0 mmole P as $NaH_2PO_4.H_2O$ kg^{-1} soil), and 2 replicates were used. Initial ionic strength was held constant by preparing P solutions in 0.03 M $KClO_4$ and pH was adjusted to 6.0 by titration with 0.5 M KOH. Two hundred mL of P solution was added to 250 mL weighed plastic centrifuge tubes containing 20.0 g of soil. The suspension was shaken reciprocally for 72 hours at 25°C and centrifuged. The supernatant solution was filtered and pH and total P determined (Asher, 1980). The tube with the sediment and residual solution was weighed. Soil in the tube was then air dried and sampled for CEC determinations.

Experiment 2. P and Zn Sorption-Desorption

Two grams of soil were equilibrated with 20 mL P solution, then with 20 mL Zn solution followed by 20 mL of 0.03 M $KClO_4$ solution, sequentially, for 72 hrs for each of the three equilibria at 25°C. Six soils, 4 P levels (0.0, 30.0, 60.0, and 90.0 mmole P kg^{-1} soil), and 5 Zn levels (0, 2.5, 5.0, 7.5 and 10.0 mmole Zn kg^{-1} soil) were assessed with 2 replicates for each treatment. Ionic strength and initial pH was adjusted as above. Suspensions were centrifuged and total P, total Zn and pH determined in the supernatant solution at the end of each equilibration. The first equilibrium determined P sorption (P_{S1}), the second Zn sorption (Zn_{S2}) and P desorption (P_{D2}) or remaining sorbed P (PS_2), the third Zn desorption (Zn_{D3}) or remaining sorbed Zn (ZnS_3) and further P desorption (P_{D3}) or remaining sorbed P (P_{S3}).

Experiment 3. Zn Fractions as Affected by Sorbed P

Samples receiving 0.0 and 90.0 mmole P kg^{-1} soil at the first equilibration and 0.0 and 10.0 mmole Zn kg^{-1} soil at the second equilibration in Experiment 2 were analyzed for Zn fractions. Solutions of 0.5 M KNO_3, 0.5 M NaOH and concentrated HNO_3+30% H_2O_2 were sequentially used to extract what has been called exchangeable Zn (Zn_{KNO3}), organic and Fe and Al oxide-associated Zn (Zn_{NaOH}) and residual Zn (Zn_{HNO3}), respectively (Levesque & Schnitzer, 1966; Emmerich et al., 1982; Sposito et al., 1982; Miller & McFee, 1983).

Results were expressed on the basis of oven dry (105°C) weight. The P_{S1}, P_{D2}, P_{D3}, Zn_{S2}, Zn_{D3} and Zn fraction values were obtained by subtracting the amount of P or Zn remaining in the solution from the total amount added or remaining from the previous step and correcting for P or Zn in the interstitial solutions. Thus sorbed P or Zn was the sum of P or Zn adsorbed on soil surfaces and P or Zn precipitated. The activity product ($\log K_{SP}$) for hopeite was calculated using the formula of $\log K_{SP} = 3 \log a_{Zn2+} + 2 \log a_{H2PO4-} + 4$ pH under the assumption that within the experimental pH range, $H_2PO_4^-$ and Zn^{2+} were the main components for P and Zn in the solution, respectively. For the conversion of concentrations into activities, the activity coefficients of $H_2PO_4^-$ and Zn^{2+} were calculated using the Debye-Huckel equation (Lindsay, 1979). Changes in CEC (Δ_{CEC}) were calculated according to the formula of $\Delta_{CEC}=CEC_P-CEC_0$, where CEC_P was the CEC of soils with added P, CEC_0 was the CEC of soils without added P.

RESULTS AND DISCUSSION

In the soils studied, increased CEC per mmole of sorbed P ranged from 0.5 to 1.05 meq (Table 2), which is consistent with the findings reported by others (Kuo & McNeal, 1984; Gillman & Fox, 1980). Over all soils, 1 mmole sorbed P resulted in 0.72 meq increase in CEC, ($\Delta_{CEC}=0.72P_{S1}$, $R^2=0.78$, $P<0.001$), which is in agreement with the average value of 0.8 meq $mmole^{-1}$ sorbed P found by Mekaru & Uehara (1972) for ferruginous tropical soils. It is also within the ranges noted for goethite by Parfitt (1978). This suggests that P reactions may have been primarily associated with Fe compounds in the soils studied, and generally agrees with accepted adsorption models (Parfitt et al., 1975; Rajan, 1975). The degree of change in CEC with sorbed P seemed to be independent of amounts of extractable Fe and Al except AO-Fe and Fe_{AM} (Table 2), which negatively correlated with the changes in CEC as affected by P_{S1}, indicating that P sorbed on amorphous materials did not contribute to increases in CEC, or the P-Fe_{AM} reaction was a precipitation. On other hand, slope values significantly correlated with original soil pH values (Table 2), suggesting that deprotonation of sorbed P occurred at high pH.

Positive correlations between P_{S1} and soil CEC, clay contents, organic C, extractable Fe and Al, and negative correlation with ZPNC (Table 3) were found. These correlations supported the speculation that P_{S1} was occurring on the edges of clay minerals and Fe crystalline compounds (Parfitt et al., 1975), such as geothite and hematite, or in reactions with organic Fe and Al materials (PP-Fe and Al). The difference between AO-Fe and PP-Fe, i.e., Fe_{AM}, was not correlated with P_{S1}, indicating that amorphous Fe oxides may not have played an important role in the process of P sorption (Lindsay, 1979).

Desorption of P was a linear function of the amount of P_{S1} within the range of 13 to 43 mmoles kg^{-1} (Fig. 1), which is consistent with the results of Barrow (1983), suggesting that the energy of P desorption was similar for every mmole of sorbed P. The decrease in slope of P_{S2} vs P_{D3} from second and third equilibria, compared to the first and second equilibria, indicated a time effect on P desorption. As the third equilibration was 72 hours later than the second, more P may have diffused into inaccessible sites or become more firmly sorbed (Moore and Zouestiagh, 1974; Barrow, 1983), thus decreasing desorption. Correlations between P_{D2} and soil characteristics (Table 3) may be a reflection of P_{S1} since P_{D2} increased with the increases in P_{S1} (Fig. 1).

Zinc addition decreased P_{D2} (Fig. 2). If the value of Zn_{S2} was greater than 9 mmoles kg^{-1} soil, there was virtually no P_{D2} from the UI and US soils. However, Zn addition did not improve the correlations between P_{D2} and soil parameters (Table 3), indicating that the effect of sorbed Zn on P_{D2} was independent of soil properties.

On the one hand, decreased P_{D2} at high Zn_{S2} levels may have been due to hopeite precipitation at high initial P and Zn rates during the second equilibration, as indicated by solubility products (Table 4) greater than that for hopeite (Lindsay, 1979). On the other hand, the evidence that Zn_{S2} increased as Zn addition rates increased at any P addition rate (Xie and MacKenzie, 1988) supports the speculation that P and Zn were sorbed at opposite ends of a spectrum of electrostatic potentials (Barrow, 1987). The Zn_{S2}-P_{D2} relationship could be evidence for a Zn-P sorption complex. This is consistent with a Zn-P specific sorption due to a Zn-P-soil complex. The importance of sorbed Zn on P desorption should be minimized since native Zn contents of soils are generally low. However, the reverse, increases in P sorption resulting in decreases in Zn desorption, is more important due to frequent P fertilizer applications in agricultural soils.

Increased Zn_{S2} was equivalent to less than 5%, in the Uplands (sand) and St.Bernard (loam) soils, and less than 1%, in the Dalhousie (clay) soils, of the increased CEC with sorbed P (Table 5), while Zn_{D3} rates were reduced 40-50% by added P at 90 mM kg^{-1} compared with zero P samples. On the average, one meq increase in CEC resulted in 1.5-3.5% decrement in Zn_{D3}. Precipitation of Zn and P as hopeite was not responsible for this effect as ion products at the third equilibration were smaller than the K_{SP} for hopeite.

Phosphate sorption improved the correlations between Zn_{S2} and DC-Fe, AO-Fe, PP-Fe or Fe_{CRY} (Table 3), suggesting that P_{S2} caused increases in Zn_{S2} on the Fe components (particularly the organic Fe, i.e., PP-Fe, and crystalline Fe). The consequence of this effect was that P_{S2} resulted in better correlations between Zn_D and soil parameters, particularly, PP-Fe and DC-Fe (Table 3), confirming the speculation that P_{S2} enhanced specific Zn sorption (Xie and MacKenzie, 1988) but mainly on Fe materials. Such materials may form precipitates with Zn and control Zn solubility (Pulford, 1986). The results that P_{S2} increased Zn_{S2} in soils (Xie and MacKenzie, 1988) were in agreement with the studies with goethite (Bolland et al., 1977), with iron and aluminum oxides (Stanton & Burger, 1970), but contrasts with the studies with soil clays (Cavallaro, 1982), and with aluminum hydroxide (McBride, 1985). Thus P_{S3} on the surface restricted Zn_{D3}, either through mechanical occlusion, increased specific adsorption sites, or enhanced negative charge effects. The bridge effect, Zn linked to the soil surface through sorbed P, was probably not significant since P_{D3} was not correlated with Zn_{D3} (Xie and MacKenzie, 1988). Kuo (1986) and Barrow (1987) also showed no evidence of the existance of the bridge effect.

The ratio of Zn_{D3} to Zn_{S2} increased with increases in Zn_{S2} (Fig. 3), indicating that with more Zn_{S2}, less energy was required to desorb Zn, or the portion of Zn specifically sorbed was lower. The higher Zn_{D3} with the coarser textured soils may have been due to a higher percent saturation of the Zn_{S2} sites in these soils. Therefore, the sorbed Zn would be held less strongly with lower energy and more Zn would be released.

Added P, compared with zero P addition, resulted in reductions in Zn_{KNO3}, but increases in Zn_{NaOH} (Xie and MacKenzie, 1988). As CEC was increased with added P, one could have expected more Zn_{KNO3} or exchangeable Zn with added P. However, the opposite was observed, indicating that Zn_{S2} did not appear as exchangeable Zn and the charge effect produced by sorbed P had little effect on Zn_{S2}. It is more likely that Zn_{S2} was associated with Fe and Al oxy-hydroxides and/or organic matter (Zn_{NaOH}), in that P addition increased the absolute values of correlation coefficients (r) between Zn fractions (particularly Zn_{NaOH}) and soil parameters (Table 6). It was shown that Zn_{KNO3} had negative, but Zn_{NaOH} and Zn_{HNO3} had positive correlations with P_{S3}. Increased positive correlations between Zn_{NaOH} and Fe or Al with P addition is consistent with the conclusion that P reacted with Fe or Al materials, increasing specific Zn sorption on these materials.

CONCLUSIONS

The effect of P addition on decreasing solution Zn in soils was shown through increasing specific Zn sorption on Fe materials. This was supported by the facts that P sorption correlated positively with organic or crystalline Fe contents, and that P sorption enhanced associations between Zn sorption (positive), Zn desorption (negative), Zn_{KNO3} (negative) or Zn_{NaOH} (positive) and Fe materials. The consequence of such reactions was a reduction in readily available Zn forms. The bridge effect, the P induced negative charge effect on Zn sorption, and precipitation of hopeite were not important mechanisms controlling soil Zn solubility in the presence of added P.

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Table 1. Selected properties of the experimental soils.

Parameter+	Soil++						Reference
	UT	US	ST	SS	DT	DS	
Classification (FAO)	Orthic-podzol		Eutric-cambisol		Humic-gleysol		1
Horizon	Ap	Bh	Ah	Bhj	Ap	Beh	
Depth (cm)	0-24	24-45	0-20	20-35	0-20	20-47	
Clay content, g kg^{-1}	100	120	200	210	410	500	2
pH, soil:water=1:2	6.3	6.4	5.5	5.4	5.7	5.7	
CEC, meq kg^{-1}	57.0	43.0	119	101	260	259	3
Organic C, g kg^{-1}	16.7	12.0	26.1	13.5	38.8	39.4	4
DC-Fe, g kg^{-1}	3.1	3.4	9.4	8.7	9.2	9.5	5
DC-Al, g kg^{-1}	1.1	1.0	1.5	1.3	1.9	1.9	5
AO-Fe, g kg^{-1}	1.5	1.3	3.7	3.1	3.1	3.1	5
AO-Al, g kg^{-1}	2.0	1.6	2.1	1.8	3.5	3.4	5
PP-Fe (Fe_{OR}), g kg^{-1}	0.5	0.4	1.3	1.1	1.4	1.4	5
PP-Al, g kg^{-1}	0.7	0.5	1.1	0.8	2.1	1.7	5
Fe_{AM}, g kg^{-1}	1.0	0.9	2.4	2.0	1.7	1.7	
Fe_{CRY}, g kg^{-1}	1.6	2.1	5.7	5.6	6.1	6.4	
P_S maxima, mmole kg^{-1}	16.6	19.1	23.9	21.8	31.7	29.9	6
ZPNC	3.2	4.2	2.5	1.7	0.6	0.4	7

\+ DC-extracted with dithionite citrate; AO-extracted with ammonium oxalate; PP-extracted with sodium pyrophosphate; ZPNC-zero point of net charge; 1-Canada Soil Survey Committee, 1978; 2-Bouyoucos, 1951; 3-Hendershot & Duquette, 1986; 4-Tabatabai & Bremner, 1970; 5-Sheldrick, 1984; 6-Olsen & Watanabe, 1957; 7-James, 1984; Fe_{AM} = (AO-Fe) - (PP-Fe); Fe_{CRY} = (DC-Fe) - (AO-Fe);

++ UT, US - Uplands top and subsoil;
ST, SS - St. Bernard top and subsoil;
DT, DS - Dalhousie top and subsoil.

Table 2. Equations of regression between cation exchange capacity (CEC) and sorbed P.

Soil+	Regression equation++	R^2	CV, %
UT	$Y= 60.4+0.94P_{S1}$	0.98^{**}	1.21
US	$Y= 44.8+1.05P_{S1}$	0.88^{**}	5.59
ST	$Y=123.6+0.49P_{S1}$	0.93^{**}	1.81
SS	$Y= 86.6+0.78P_{S1}$	0.98^{**}	2.08
DT	$Y=278.1+0.86P_{S1}$	0.91^{**}	1.38
DS	$Y=262.4+0.77P_{S1}$	0.98^{**}	0.70
Overall soils	$\Delta_{CEC}=0.72P_{S1}$	0.78^{**}	
	Simple linear correlation (r)		
Slope vs AO-Fe		-0.87^{*}	
Fe_{AM}		-0.93^{**}	
pH		0.87^{*}	
others[1)]		ns	

\+ UT, US - Uplands top and subsoil; ST, SS - St. Bernard top and subsoil; DT, DS - Dalhousie top and subsoil;

++ $Y=CEC$, meq kg^{-1} soil; P_{S1} = P sorption mmole kg^{-1}; pairs of data used for regression of each soil are 10;

1) other parameters shown in Table 1;

ns not significant;

* significant at the level of $p<0.05$;

** significant at the level of $p<0.01$.

Table 3. Linear correlation coefficients (r) between P sorption (P_{S1}), P desorption (P_{D2}), Zn sorption (Zn_{S2}) or Zn desorption (Zn_{D3}) and soil properties.

Parameter+	P_{S1}	P_{D2} 1)		Zn_{S2} 2)		Zn_{D3} 2)	
		-Zn	+Zn	-P	+P	-P	+P
	r						
Clay content	0.97^{**}	0.97^{**}	0.72^{*}	0.89^{*}	$0.80^{\pounds}$	-0.83^{*}	-0.96^{**}
CEC	0.96^{**}	0.99^{**}	0.96^{**}	0.95^{**}	0.88^{*}	-0.90^{*}	-0.99^{**}
Organic C	0.92^{**}	0.94^{**}	0.94^{**}	0.98^{**}	0.91^{*}	-0.98^{**}	-0.97^{**}
DC-Fe	0.82^{*}	0.81^{*}	0.86^{*}	$0.78^{\pounds}$	0.83^{*}	ns	$-0.77^{\pounds}$
DC-Al	0.96^{**}	0.99^{**}	0.99^{**}	0.98^{**}	0.94^{**}	-0.91^{**}	-0.99^{**}
AO-Fe	ns	ns	$0.78^{\pounds}$	ns	0.81^{*}	ns	ns
AO-Al	0.89^{*}	0.95^{**}	0.91^{*}	0.93^{**}	0.84^{*}	-0.94^{**}	-0.97^{**}
PP-Fe (Fe_{OR})	0.88^{*}	0.89^{*}	0.94^{**}	0.88^{*}	0.92^{**}	$-0.74^{\pounds}$	-0.87^{*}
PP-Al	0.91^{*}	0.96^{**}	0.95^{**}	0.97^{**}	0.90^{*}	-0.93^{**}	-0.98^{**}
Fe_{AM}	ns	ns	ns	ns	ns	ns	ns
Fe_{CRY}	0.86^{*}	0.84^{*}	0.88^{*}	$0.80^{\pounds}$	0.82^{*}	ns	$-0.81^{\pounds}$
ZPNC	-0.87^{*}	-0.96^{**}	-0.95^{**}	-0.85^{*}	-0.87^{*}	$0.78^{\pounds}$	0.94^{*}

\+ DC-extracted with dithionite citrate;
AO-extracted with ammonium oxalate;
PP-extracted with sodium pyrophosphate.
Fe_{AM} = (AO-Fe) - (PP-Fe), i.e., amorphous Fe;
Fe_{CRY} = (DC-Fe) - (AO-Fe), i.e., crystalline Fe;

1) -Zn without added Zn, +Zn with added Zn at 10 mmole Zn kg^{-1};
2) -P without added P, +P with added P at 90 mmole P kg^{-1};
ns not significant; £ significant at $p<0.10$;
* significant at $p<0.05$; ** significant at $p<0.01$.

Table 4. Treatments associated with activity products greater than $\log K_{SP}$ (3.8) for hopeite at the second equilibration.

Initial rate		Soil+					
P	Zn	UT	US	ST	SS	DT	DS
(mmole kg^{-1})							
				$\log K_{SP}$			
30	5.0	-	-	-	5.44	3.99	-
30	7.5	4.13	-	4.32	5.59	4.53	4.12
30	10.0	5.68	3.82	4.90	5.97	5.03	4.52
60	7.5	-	3.88	-	5.08	3.95	-
60	10.0	-	-	4.39	5.83	4.41	3.94
90	7.5	-	-	-	4.64	-	-
90	10.0	-	4.33	-	5.30	4.18	4.01

+ UT, US - Uplands top and subsoil; ST, SS - St. Bernard top and subsoil; DT, DS - Dalhousie top and subsoil; the dashes indicates values < 3.80.

Table 5. Sorbed P (P_{S1}), changes in cation exchange capacity (Δ_{CEC}), sorbed Zn (Zn_{S2}) and desorbed Zn (Zn_{D3}) as a function of added P (initial Zn rate=5 mmole kg^{-1}).

Initial P rate	P_{S1}	Δ_{CEC}	Average Zn_{S2}	Zn_{S2} as a proportion of Δ_{CEC}+	Zn_{D3} as a proportion of Zn_{S2}
(mmole kg^{-1})		(meq kg^{-1})	(mmole kg^{-1})	(%)	(%)
			UT++		
0.0	0.00	0.0	4.39	-	3.0
30.0	11.15	11.7	4.65	4.4	2.3
60.0	12.63	12.2	4.70	5.1	2.1
90.0	14.75	16.2	4.73	4.2	1.8
$LSD_{0.05}$	-	-	0.02	-	0.3
			US		
0.0	0.00	0.0	4.16	-	3.5
30.0	14.13	16.0	4.48	4.0	2.6
60.0	15.40	20.3	4.58	4.2	2.5
90.0	15.74	23.1	4.66	3.5	2.2
$LSD_{0.05}$	-	-	0.04	-	0.6
			ST		
0.0	0.00	0.0	4.61	-	3.0
30.0	15.33	12.6	4.75	3.8	2.2
60.0	19.44	14.5	4.81	3.8	1.9
90.0	24.20	17.0	4.84	3.5	1.6
$LSD_{0.05}$	-	-	0.04	-	0.2
			SS		
0.0	0.00	0.0	4.31	-	4.2
30.0	12.73	13.4	4.57	3.9	3.0
60.0	20.09	14.0	4.66	5.0	2.5
90.0	22.71	20.4	4.70	3.8	1.9
$LSD_{0.05}$	-	-	0.03	-	0.5
			DT		
0.0	0.00	0.0	4.80	-	1.3
30.0	14.87	13.0	4.83	0.5	1.1
60.0	21.63	21.7	4.83	0.4	1.0
90.0	28.89	34.0	4.88	0.5	0.7
$LSD_{0.05}$	-	-	0.03	-	0.2
			DS		
0.0	0.00	0.0	4.74	-	2.2
30.0	16.74	18.2	4.82	0.9	1.5
60.0	22.84	24.0	4.85	0.9	1.2
90.0	31.31	33.3	4.87	0.8	1.0
$LSD_{0.05}$	-	-	0.03	-	0.3

+ calculated as $(Zn_P-Zn_0)\times2\times100/((\Delta_{CEC})_i$, $Zn_P=Zn_{S2}$ with added P, $Zn_0=Zn_{S2}$ without added P, i=P rate;

++ UT, US - Uplands top and subsoil; ST, SS - St. Bernard top and subsoil; DT, DS - Dalhousie top and subsoil.

Table 6. Linear correlation coefficients (r) between Zn fractions and soil properties.

Parameter^{+}	Zn fraction					
	Zn_{KNO3}		Zn_{NaOH}		Zn_{HNO3}	
	$-P^{++}$	$+P^{++}$	$-P$	$+P$	$-P$	$+P$
	r					
Clay content	ns	-0.92^{**}	ns	0.93^{**}	0.86^{*}	0.92^{**}
CEC	-0.82^{*}	-0.97^{**}	ns	0.95^{**}	0.94^{**}	0.97^{**}
Organic C	-0.85^{*}	-0.99^{**}	0.85^{*}	0.93^{**}	0.95^{**}	0.98^{**}
DC-Fe	ns	ns	ns	0.89^{*}	ns	ns
DC-Al	ns	-0.99^{**}	ns	0.99^{**}	0.97^{**}	0.99^{**}
AO-Fe	ns	ns	ns	0.81^{*}	ns	ns
PP-Fe	ns	-0.88^{*}	ns	0.96^{**}	0.89^{*}	0.88^{*}
PP-Al	-0.83^{*}	-0.97^{**}	0.87^{*}	0.93^{**}	0.98^{**}	0.98^{**}
Fe_{AM}	ns	ns	ns	ns	ns	ns
Fe_{CRY}	ns	$-0.79^{£}$	ns	0.91^{*}	0.81^{*}	$0.80^{£}$
ZPNC	ns	0.89^{*}	ns	-0.92^{**}	-0.87^{*}	-0.90^{*}
P_{S3}	-	-0.85^{*}	-	0.91^{*}	-	0.85^{*}

$+$ DC -extracted with dithionite citrate;
AO -extracted with ammonium oxalate;
PP -extracted with sodium pyrophosphate;
Fe_{AM} = (AO-Fe) - (PP-Fe), i.e., amorphous Fe;
Fe_{CRY} = (DC-Fe) - (AO-Fe), i.e., crystalline Fe;
P_{S3} -P remaining sorbed at the third equilibration;
$++$ -P without added P, +P with added P at 90 mmole P kg^{-1};
ns not significant; £ significant at $p<0.10$;
* significant at $p<0.05$; ** significant at $p<0.01$.

Fig. 1. Phosphate desorption at the second or the third equilibration as affected by P sorbed at the first or the second equilibration. □ P desorbed at the second equilibration verses P sorbed at the first equilibration, $P_{D2}=-1.76+0.21P_{S1}$, $r^2=0.84^{**}$; + P desorbed at the third equilibration verses P sorbed at the second equilibration, $P_{D3}=-0.84+0.14P_{S2}$, $r=0.83^{**}$.

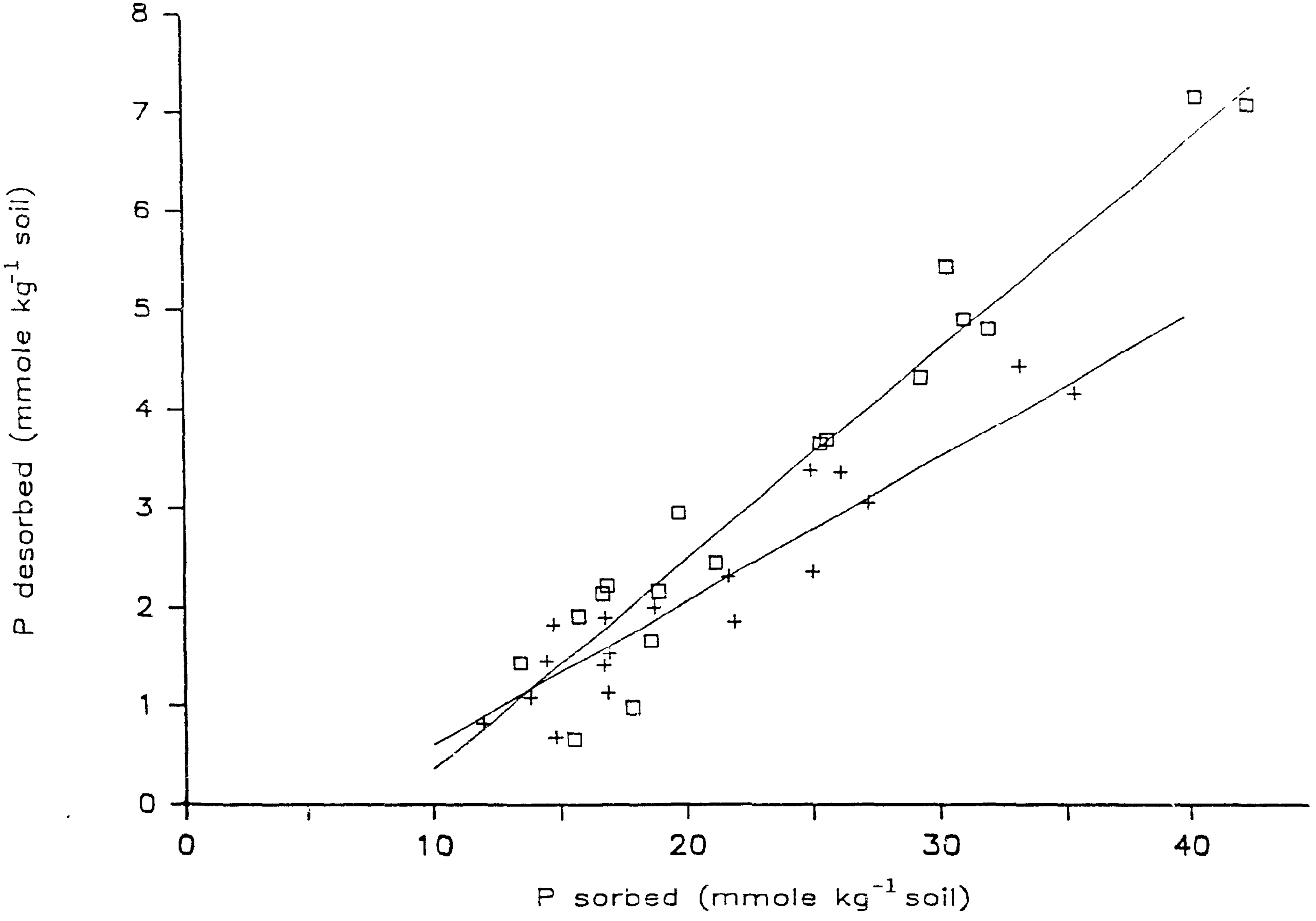
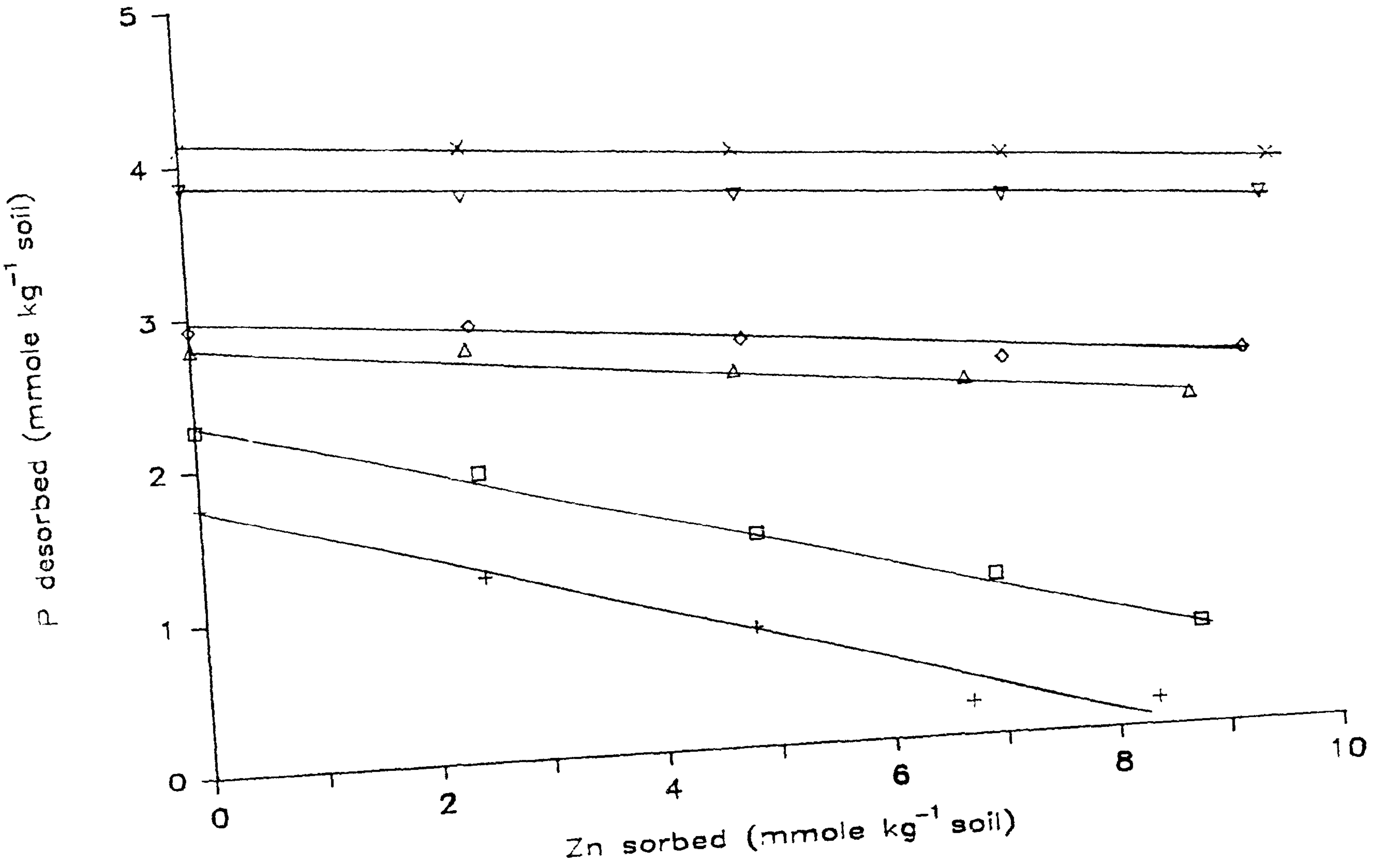

P desorbed (mmole kg^{-1} soil)
8
7
6
5
4
3
2
1
0
0
10
20
30
40
P sorbed (mmole kg^{-1} soil)

Fig. 2. Relationship between Zn sorption (Zn_{S2}) and P desorption (P_{D2}) during the second equilibration. Soils: ^ DT, ▽ DS, ◇ ST, △ SS, □ UT, and + US.

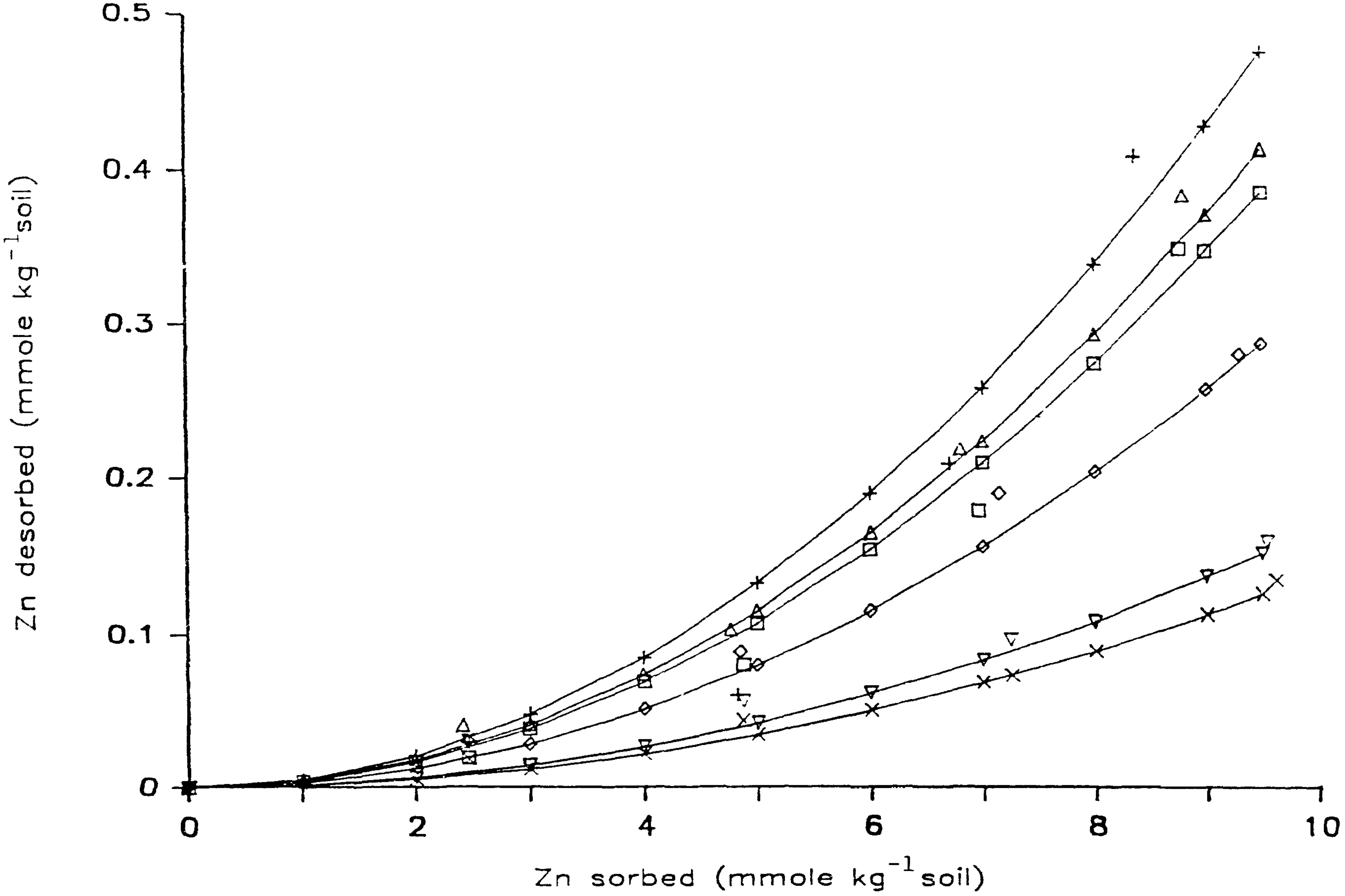
Soil	Regression	r^2	Soil	Regression	r^2
DT	P_{D2}=4.12-0.0437Zn_{S2}	0.995**;	DS	P_{D2}=3.84-0.0437Zn_{S2}	0.985**
ST	P_{D2}=2.94-0.0581Zn_{S2}	0.993**;	SS	P_{D2}=2.83-0.0735Zn_{S2}	0.983**
UT	P_{D2}=2.31-0.1843Zn_{S2}	0.997**;	US	P_{D2}=1.73-0.1992Zn_{S2}	0.975**



5
4
3
2
1
0
P desorbed (mmole kg^{-1} soil)
0
2
4
6
8
10
Zn sorbed (mmole kg^{-1} soil)

Fig. 3. Effect of sorbed Zn (Zn_{S2}) at the second equilibration on Zn desorption (Zn_{D3}) at the third equilibration. Soils: X DT, ∇ DS, ◇ ST, △ SS, □ UT, and + US.

Soil	Regression	r^2	Soil	Regression	r^2
DT	$Zn_{D3}=0.0014(Zn_{S2})^2$	0.82**	DS	$Zn_{D3}=0.0017(Zn_{S2})^2$	0.76**
ST	$Zn_{D3}=0.0032(Zn_{S2})^2$	0.85**	SS	$Zn_{D3}=0.0046(Zn_{S2})^2$	0.79**
UT	$Zn_{D3}=0.0043(Zn_{S2})^2$	0.89**	US	$Zn_{D3}=0.0053(Zn_{S2})^2$	0.76**


0.5
0.4
0.3
0.2
0.1
0
Zn desorbed (mmole kg^{-1}soil)
0
2
4
6
8
10
Zn sorbed (mmole kg^{-1}soil)

CONNECTING PARAGRAPH

In the previous chapter, sorbed orthophosphate (OP) was demonstrated to increase soil CEC and to decrease Zn solubility through enhanced specific Zn sorption on particle surfaces of non-autoclaved soils.

Pyrophosphate (PP) is used as a P fertilizer, yet it has potential for sequestering Zn in solution. However, two reactions of PP in soils may limit this sequestering effect: a rapid hydrolysis of PP to OP, and PP sorption. The following chapter reports studies in which PP was added to autoclaved soils to test the hypothesis that PP sorption would increase soil CEC, create sorption sites for Zn, and change characteristics of sorption, desorption and fraction distribution of added Zn.

CHAPTER III

EFFECTS OF SORBED PYROPHOSPHATE ON THE ZINC STATUS OF THREE AUTOCLAVED SOILS OF EASTERN CANADA

INTRODUCTION

Pyrophosphate (PP) has several kinds of reactions in soils: (1) it undergoes rapid hydrolysis to orthophosphate (Blanchar and Hossner, 1969; Busman and Tabatabai, 1985; Parent and MacKenzie, 1985; Dick and Tabatabai, 1986); (2) it is sorbed by soil components in large quantities (Blanchar and Hossner, 1969; Sutton and Larsen, 1964; Mnkeni and MacKenzie, 1985; Juo and Maduakor, 1973); (3) it dissolves sorbed organic materials in soils (Mnkeni and MacKenzie, 1985; Mortvedt and Osborn, 1977); (4) it forms complexes with Fe, Al, and Mn in solution, and has been used in extracting soil organic Fe, Al or Mn (Sheldrick, 1984, McKeague, 1967); (5) it sequesters micronutrients, such as Zn^{2+}, and keeps nutrients in solution (Mortvedt and Osborn, 1977; Giordano et al., 1971; Bar-Yosef and Asher, 1983; Slack et al., 1965). These reactions can affect Zn solubility directly or indirectly.

The efficiency of PP in sequestering Zn depends on the reactions of PP in soils. Although dissolution of organic matter and sequestration of Zn caused by PP addition increased Zn solubility (Mortvedt and Osborn, 1977), such increased Zn did not appear to play an important role in Zn nutrition of crops, especially in calcareous soils. This was probably due to PP hydrolysis and orthophosphate (OP) induced Zn deficiency for crop growth (Singh and Dartiques, 1970; Hashimoto and Wakefield, 1974; Schield et al., 1978; Rehm et al., 1980). Lehr et al. (1967) showed that PP could decrease Zn concentration in soil solution through forming $Zn-NH_4-PP$ precipitates. In this case, monoammonium phosphate was found to be more effective than ammonium pyrophosphate if Zn was limiting, because greater P uptake from ammonium pyrophosphate antagonized Zn uptake resulting in poor corn growth (Adriano and Murphy, 1970).

Mechanisms of crop Zn deficiency associated with PP applications are not well understood due to the lack of information on Zn transformations in soil as affected by sorbed PP. Mechanisms involved in increases in Zn sorption with PP sorption could be both physical and chemical. Physical mechanisms include a "coulombic effect", provided PP sorption results in increases in soil cation exchange capacity (CEC) or surface negative charges. Increased Zn sorption may be due to a "bridge effect", where Zn^{2+} ions attach to sorbed PP. Chemical mechanisms include precipitation, where PP, Fe, Al or other ions form precipitates with Zn^{2+} ions, and "specific sorption", where PP sorption changes surface properties to enhance Zn sorption. It is speculated that sorbed PP may form complexes with Zn if two or more oxygens of sorbed PP are free to form bonds with Zn. Other mechanisms include exposure of more surfaces for Zn sorption due to increased dissolutions by the added PP of organic matter, Fe, Al, and Mn.

The objectives of this study were to investigate the effect of PP sorption on soil CEC, and on Zn sorption, desorption and fraction distribution in soils in order to evaluate the impact of sorbed PP on mechanisms of Zn reactions.

MATERIALS AND METHODS

Soil Pretreatments

Top (T) and subsoil (S) samples were obtained from cultivated Uplands (U) and Dalhousie (D) soils and a pastured St.Bernard (S) soil from southwestern Quebec, Canada, indicated as UT, US, DT, DS, ST and SS. Soils were selected to represent the major agricultural soils of the region; those developed on alluvial, marine-lacustrine and glacial till deposits, respectively (Table 1, Chapter II). Samples were air dried, ground to <1 mm and autoclaved for one h a day at 121°C and 15 kPa for three days at a moisture content of 0.33 kPa suction. Autoclaved samples were then air dried and analyzed for CEC, organic C, dithionite-citrate extractable Fe and Al (DC-Fe and DC-Al), ammonium oxalate-extractable Fe and Al (AO-Fe and AO-Al), and sodium pyrophosphate-extractable Fe and Al (PP-Fe and PP-Al) using methods noted in Chapter II. In general, clay, organic C and extractable Fe and Al increased in the order of Uplands, St.Bernard and Dalhousie (Table 1) but Fe_{AM} was lower in Dalhousie than in St.Bernard soils. Compared to non autoclaved soils (Table 1, Chapter II), autoclaved soils had reduced DC-Fe, organic complexed (Fe_{OR}, PP-extractable), and crystalline Fe (Fe_{CRY}, difference between DC-and AO-extractalbe Fe), reduced DC, AO and PP extractable Al and increased ratio of Fe_{CRY}/Fe_{AM} while values of Fe_{AM} were unchanged.

Equilibrium Solutions

Solutions containing either PP as $Na_4P_2O_7.10H_2O$ or Zn as $ZnSO_4.7H_2O$ were prepared in 0.03 M $KClO_4$. Solutions were prepared in deionized distilled water under sterile conditions (autoclaved containers or apparatus, micro filters, ect.). Solution pH values were adjusted to 6.0 with 0.5 N KOH after addition to soil samples, and 20 drops of toluene were added to 200 mL suspension (or 2 drops for 20 mL). Weight of the soil suspension was recorded before and after each addition of solution or reagent.

Experiment 1. PP Sorption and Soil CEC

Experimental procedures were similar to those outlined for

Experiment 1 of Chapter II, except that soil samples were autoclaved before the addition of PP solutions and operations was carried out under sterile conditions. The supernatant solution was filtered and analyzed for orthophosphate (OP) (Asher, 1980) and total P after hydrolysis (H_2SO_4 at 95°C for 15 min) (Asher and Bar-Yosef, 1982). Thus P concentration as PP was the difference between total P and OP concentration. Changes in CEC (Δ_{CEC}) were calculated according to Δ_{CEC}=CEC_{PP}-CEC_0, where CEC_{PP} was the CEC of soils with added PP, CEC_0 was the CEC of soils without added PP. Regression equations relating CEC to sorbed PP (PP_{S1}) were calculated (Steel and Torrie, 1980).

Experiment 2. PP Sorption and Zn Sorption-desorption

Three equilibrations between PP, Zn or 0.03 M $KClO_4$ solutions and soil samples were carried out. Experimental procedures outlined for Experiment 2 of Chapter II were followed, except that soil samples were autoclaved before the addition of PP solutions. Treatments were duplicated. The supernatant solutions from each of the three equilibrations were filtered and analyzed for pH, concentrations of OP and total P after hydrolysis, and Zn. Phosphate concentration as PP was calculated by the difference between total P and OP. The first equilibrium determined PP sorption (PP_{S1}); the second Zn sorption (Zn_{S2}), PP desorption (PP_{D2}) or remaining sorbed PP (PP_{S2}); the third Zn desorption (Zn_{D3}), remaining sorbed Zn (Zn_{S3}), further PP desorption (PP_{D3}), and remaining sorbed PP (PP_{S3}). Corrections were made for interstitial PP or Zn carried from previous equilibrations.

Experiment 3. Zn Fractions as Affected by Sorbed PP

Samples receiving 0.0 and 90.0 mmole P kg^{-1} soil at the first equilibration and 0.0 and 10.0 mmole Zn kg^{-1} soil at the second equilibration (Experiment 2) were analyzed for Zn fractions. Twenty five ml of 0.5 M KNO_3, then of 0.5 M NaOH solutions, and finally 15 ml concentrated HNO_3+30% H_2O_2 at 110°C were sequentially used to extract exchangeable Zn (Zn_{KNO3}), organic and Fe or Al oxide-associated Zn (Zn_{NaOH}) and residual Zn (Zn_{HNO3}), (Levesque and Schnitzer, 1966; Emmerich et al., 1982; Sposito et al., 1982; Miller and McFee, 1983).

Results were expressed on the basis of oven-dry (105°C) soil weight. The solution OP concentration was less than 0.5% of total P concentration in the three equilibria, and P or Zn parameters (sorption-desorption) were not related to OP concentration, so it was assumed that P concentration was equal to total P concentration. Statistical analysis of the experimental data was based on analysis of variance involving a randomized complete block design and differences among means were analyzed using the methods of least significant difference (Steel and Torrie, 1980).

RESULTS AND DISCUSSION

Sorbed PP and CEC

Regression equation indicated that PP sorption increased soil CEC in a linear manner (Table 2) with slopes ranging from 0.52 to 0.89 mmole(+), or 0.052 to 0.089 cmol(+), per mmole sorbed P. Slopes tended to be greater with increases in contents of clay, extractable-Fe or Al, and organic C, and were correlated with the ratios of clay to or crystalline Fe (Fe_{CRY}, difference between DC-Fe and AO-Fe, Table 1) to amorphous Fe (Fe_{AM}, difference between AO-Fe and PP-Fe) but not with Fe_{AM} (Table 2). The non-significant relationship between slope and Fe_{AM}

may have been associated with reaction products of PP with Fe_{AM} (Lindsay, 1979) making no contribution to increases in CEC.

At the same level of PP addition, amounts of PP sorption increased in the order Uplands, St.Bernard and Dalhousie soils (Table 3), and the same was true for CEC or for change in CEC (Δ_{CEC}). There existed significant linear correlations between soil clay, organic C, PP-Fe (organic-Fe) or Fe_{CRY} contents and PP sorption (Table 4) while the correlation between PP_{S1} and Fe_{AM} was not significant. These results suggest that PP sorption and Δ_{CEC} were associated with Fe_{CRY}, the dominant Fe form in the finer textured soils, and that PP sorption was less important in increasing CEC on soils high in Fe_{AM} content.

Zn Sorption as Affected by PP

Zinc sorption was increased in the presence of sorbed PP (Table 3). The higher the rate of PP addition, the more Zn was sorbed, indicating that solution PP did not increase Zn solubility through sequestering, perhaps because PP did not reach a hypothetical threshold concentration required for sequestration (Bar-Yosef and Asher, 1983).

Two aspects, sorbed Zn in relation to increased CEC, and to exchangeable-Zn, need to be examined to see whether the coulombic effect was in operation. If there existed a coulombic effect, then sorbed Zn should be in positive proportion to soil CEC, and this was true (Table 3). However, the increased Zn_{S2} was only a small fraction of the increased CEC caused by sorbed PP (Table 3), and was equivalent to 7 to 12% of the Δ_{CEC} in the Uplands, but only 0.3-2.8% of the Δ_{CEC} in the St.Bernard and the Dalhousie soils. The coulombic effect, if it exists, was limited, but relatively more important in the coarser than in the finer textured soils. Exchangeable Zn (Zn_{KNO3}) should be greater in the presence of sorbed PP compared to zero PP treatment if the coulombic effect was in operation. Experimental results did not fulfill this criterion (Table 5). The amounts of Zn_{KNO3} with PP sorption were 41-56% of those with zero PP in all except the US soil. The conclusion that increases in Zn sorption with sorbed P were not due to the coulombic effect was in agreement with results for OP in Chapter II. The sorbed P, by increasing surface negative charges, may have enhanced the movement of Zn ions to the soil surface, under the drive of electrostatic attraction, where Zn was eventually specifically sorbed.

The bridge effect would suggest that PP_{D3} should be positively correlated with Zn_{D3}. Experimental data did not show this tendency (unpublished data), indicating that the bridge effect was not significant in spite of the fact that added Zn did enhance correlations between PP_{D2} and some soil parameters (Table 4).

The first equilibration between PP solution and the soil removed active components, such as Fe, Al and Si and solublized organic matter (Sheldrick, 1984; Mnkeni and MacKenzie, 1985). The remaining active components, including PP, which may form precipitates or complexes with Zn, were well below the levels required for precipitation to occur during the second equilibrium (Lindsay, 1979).

Pyrophosphate sorption most likely resulted in increased specific Zn sorption by formation of a Zn-PP-soil complex. This was evidenced by the following results:

(1) Sorbed PP decreased both Zn_{D3} (Figs. 1, 2, and 3) and the percent of Zn_{D3} (Table 3). Significant effects of PP sorption on reduced

percent in Zn_{D3} were observed in the Uplands and St.Bernard soils (Table 3). At a fixed level of sorbed Zn, desorbed Zn with zero PP treatments was twice as much as that with sorbed PP, greater in the sub- than in the top-soil samples, and more significant in the coarser than in finer textured soils (Figs. 1, 2 and 3). This suggested that PP sorption was more effective in increasing Zn sorption in coarser than in finer textured soils. This may be due to potential-specific sorption sites being less numerous in coarser than in finer textured soils, or due to lower organic matter, and less coating of sorption sites. On the other hand, relatively more Zn_{D3} at higher levels of Zn_{S2} suggested that the energy required for Zn sorption was reduced with increases in the fraction of the surface covered by Zn, and sorbed PP increased the energy needed for Zn desorption, particularly in the coarser textured soils.

(2) Added Zn decreased PP desorption and enhanced the associations between PP_{D2} and organic C, CEC, and all Fe fractions except Fe_{AM} (Table 4). This would appear to indicate that Zn-PP complex sorbed on soil surfaces through Fe or organic compounds.

(3) More added Zn was distributed as Zn_{NaOH} and Zn_{HNO3} in soils with added PP compared with zero PP (Table 5). The Zn_{NaOH} with added PP was two to three times that with zero PP treatments in the Uplands and in the St.Bernard soils, while being about equal in the Dalhousie soils (Table 5), indicating that added PP significantly increased Zn complexation by Fe or organic materials in the soil.

(4) Correlations between Zn_{NaOH} and CEC, Al, clay and organic C disappeared in the presence of sorbed PP, indicating that added PP

disrupted soil surfaces and, removed organic C (Mnkeni and MacKenzie, 1985) to an extent that Zn_{NaOH} was increased (Table 5). Such increases were not related to measured soil variables, perhaps due to creation of an excess of sorption sites.

(5) Significant positive correlations existed between Zn_{HNO3} and PP_{S3} (Table 6). Thus sorbed PP was a major factor in increasing Zn_{NaOH} and Zn_{HNO3} since these two Zn fractions were increased in the presence of sorbed PP (Table 5).

(6) The increased Zn specific sorption (Zn_{S3}-Zn_{KNO3}) by PP addition was most obvious in the Uplands and the St.Bernard soils, and was more pronounced in the subsoil than in the topsoil (Table 5). Increases in contents of organic C, clay, and PP-Fe (organic Fe) and extractable-Al reduced PP effects on increasing specific Zn sorption as indicated by negative values of correlation coefficients (Table 7). This suggests that these variables may have reduced the ability of PP to enhance specific Zn sorption.

CONCLUSIONS

Increased solution PP did not enhance Zn solubility, but sorbed PP increased Zn sorption. The mechanism involved a complex reaction of PP, Zn and soil components, rather than an increase in exchangeable Zn with added PP, precipitation, or a "bridge" effect. This is supported by the following evidence (1) that PP addition increased CEC but reduced KNO_3-extractable Zn (exchangeable); (2) that a "bridge" effect was not evident, and solubility products of Zn-PP and other complexes were not exceeded; and (3) that sorbed PP decreased Zn desorption probably through increasing the energy needed for Zn desorption, and increased

0.5 N NaOH and concentrated HNO_3-extractable Zn, or Zn associated with Fe, Al, or organic matter. Thus in spite of the fact that PP has the ability to complex cations, dissolve organic matter, and increase CEC, PP still sorbs strongly on soil particle surfaces, and resulted in changes in soil properties which significantly enhanced specific Zn sorption.

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Table 1. Selected properties of the autoclaved soils.

Parameter+	Soil						Reference
	UT^{++}	US	ST	SS	DT	DS	
CEC, meq kg^{-1}	54.9	37.4	129	111	312	307	1
OrganicC, g kg^{-1}	7.4	3.8	25.4	14.3	39.5	31.6	2
DC-Fe, g kg^{-1}	2.6	3.1	7.7	7.3	7.7	8.0	3
-Al, g kg^{-1}	0.8	0.8	1.0	0.9	1.5	1.4	3
AO-Fe, g kg^{-1}	1.8	1.4	3.3	2.6	2.7	2.8	3
-Al, g kg^{-1}	1.8	1.5	1.6	1.3	3.1	3.2	3
PP-Fe, g kg^{-1}	0.3	0.2	0.9	0.6	1.0	1.2	3
-Al, g kg^{-1}	0.3	0.3	0.4	0.5	1.2	1.5	3
Fe_{AM}, g kg^{-1}	1.5	1.2	2.4	2.0	1.7	1.6	
Fe_{CRY}, g kg^{-1}	0.8	1.7	4.4	4.7	5.0	5.2	
Fe_{CRY}/Fe_{AM}	0.5	1.4	1.8	2.4	2.9	3.3	

\+ DC-extracted with dithionite citrate; AO-extracted with ammonium oxalate; PP-extracted with sodium pyrophosphate; 1-Hendershot & Duquette, 1986; 2-Tabatabai & Bremner, 1970; 3-Sheldrick, 1984;
Fe_{AM} is difference between AO-Fe and PP-Fe;
Fe_{CRY} is difference between DC-Fe and AO-Fe;
Other values of parameters are in Chaper II;

++ UT, US - Uplands top and subsoil;
ST, SS - St. Bernard top and subsoil;
DT, DS - Dalhousie top and subsoil.

Table 2. Regression equations relating cation exchange capacity (CEC) of autoclaved soils and sorbed pyrophosphate (PP).

Soil+	Regression equation	R^2	CV, %
UT	$CEC = 57.3 + 0.52\ PP_{S1}$ ++	0.91^{***}	4.4
US	$CEC = 43.8 + 0.62\ PP_{S1}$	0.95^{***}	4.2
ST	$CEC = 128 + 0.70\ PP_{S1}$	0.97^{***}	2.2
SS	$CEC = 104 + 0.64\ PP_{S1}$	0.85^{***}	6.7
DT	$CEC = 290 + 0.83\ PP_{S1}$	0.98^{***}	1.1
DS	$CEC = 276 + 0.89\ PP_{S1}$	0.98^{***}	1.1
	Simple linear correlations (r)		
Slope	vs Fe_{OR} (PP-Fe)	0.91^{*}	
	vs Fe_{CRY}	0.83^{*}	
	vs Fe_{AM}	ns	
	vs Organic C	0.89^{*}	
	vs Clay	0.97^{**}	
	vs Fe_{CRY}/Fe_{AM}	0.93^{**}	
	vs Clay/Fe_{AM}	0.92^{**}	
	vs DC-Al	0.94^{**}	
	vs AO-Al	0.84^{*}	
	vs PP-Al	0.93^{**}	
	vs others	ns	

\+ UT, US - Uplands top and subsoil; ST, SS - St. Bernard top and subsoil; DT, DS - Dalhousie top and subsoil;
Fe_{CRY} - difference between DC-Fe and AO-Fe, i.e., crystalline Fe;
Fe_{AM} - difference between AO-Fe and PP-Fe, i.e., amorphous Fe;
where DC- extracted with dithionite citrate;
AO- extracted with ammonium oxalate;
PP- extracted with sodium pyrophosphate;

++ CEC, mmole(+) kg^{-1} soil; PP_{S1} = P sorption, mmole P kg^{-1}; 10 pairs of data used for regression of each soil;

ns Not significant; * Significant at $p < 0.05$;

** Significant at $p < 0.01$; *** Significant at $p < 0.0001$.

Table 3. Sorbed pyrophosphate (PP_{S1}), changes in cation exchange capacity (Δ_{CEC}), sorbed Zn (Zn_{S2}) and desorbed Zn (Zn_{D3}) as a function of added pyrophosphate (initial Zn rate= 5 mmole kg^{-1}).

Initial PP rate	PP_{S1}	Δ_{CEC}	Average Zn_{S2}	Zn_{S2} as a proportion of Δ_{CEC} 1)	Zn_{D3} as a proportion of Zn_{S2}
mmole P kg^{-1}		mmole(+) kg^{-1}	mmole kg^{-1}	-------- %	--------
			Uplands topsoil (UT)		
0.0	0.0	-	3.87	-	5.5
30.0	21.1	14.1	4.37	7.1	4.7
60.0	31.8	18.7	4.54	7.2	3.8
90.0	46.3	21.0	4.62	7.1	4.0
$LSD_{0.05}$	-	-	0.06	-	0.9
			Uplands subsoil (US)		
0.0	0.0	-	3.21	-	9.7
30.0	21.7	15.4	4.14	12.1	5.6
60.0	28.8	20.3	4.29	10.6	5.7
90.0	42.5	23.7	4.33	9.5	5.0
$LSD_{0.05}$	-	-	0.05	-	1.3
			St.Bernard topsoil (ST)		
0.0	-1.9	-	4.24	-	5.0
30.0	24.0	19.0	4.40	1.7	3.6
60.0	45.1	34.8	4.57	1.9	3.0
90.0	64.6	41.7	4.64	1.9	2.8
$LSD_{0.05}$	-	-	0.03	-	0.7
			St.Bernard subsoil (SS)		
0.0	-0.4	-	4.06	-	5.7
30.0	25.4	21.1	4.35	2.7	3.4
60.0	46.7	37.6	4.56	2.7	2.8
90.0	72.0	42.0	4.65	2.8	2.7
$LSD_{0.05}$	-	-	0.05	-	0.8
			Dalhousie topsoil (DT)		
0.0	-0.3	-	4.78	-	1.6
30.0	26.5	22.4	4.99	1.9	2.0
60.0	54.4	48.7	4.90	0.5	1.5
90.0	80.6	64.5	4.87	0.3	1.5
$LSD_{0.05}$	-	-	ns	-	ns
			Dalhousie subsoil (DS)		
0.0	-0.3	-	4.73	-	1.7
30.0	27.1	24.6	4.81	0.7	1.5
60.0	54.3	46.8	4.86	0.6	1.7
90.0	82.0	74.5	4.88	0.4	1.5
$LSD_{0.05}$	-	-	0.05	-	ns

1) calculated as $(Zn_{PP}-Zn_{0})x2x100/(\Delta_{CEC})_{i}$, $Zn_{PP}=Zn_{S2}$ with added PP, $Zn_{0}=Zn_{S2}$ without added PP, i=P rate.

Table 4. Linear correlation coefficients (r) between pyrophosphate (PP) sorption (PP_{S1}), PP desorption (PP_{D2}), Zn sorption (Zn_{S2}) or Zn desorption (Zn_{D3}) and properties of autoclaved soils.

Parameter^{+}	PP_{S1}	$PP_{D2}$$^{1)}$		$Zn_{S2}$$^{2)}$		$Zn_{D3}$$^{2)}$	
		-Zn	+Zn	-PP	+PP	-PP	+PP
	r						
Clay^{++}	0.89^{*}	ns	ns	0.81^{*}	0.88^{*}	-0.94^{**}	-0.83^{*}
CEC	0.90^{*}	ns	$0.80^{\pounds}$	0.88^{*}	0.93^{**}	-0.98^{**}	-0.89^{*}
Organic C	0.88^{*}	ns	0.93^{**}	0.91^{*}	0.91^{*}	-0.95^{**}	-0.94^{**}
DC-Fe	0.92^{**}	ns	0.92^{**}	0.81^{*}	$0.75^{\pounds}$	$-0.73^{\pounds}$	-0.90^{*}
DC-Al	0.86^{*}	ns	$0.78^{\pounds}$	0.84^{*}	0.91^{*}	-0.96^{**}	-0.88^{*}
AO-Fe	$0.77^{\pounds}$	ns	0.91^{*}	$0.79^{\pounds}$	ns	ns	$-0.76^{\pounds}$
AO-Al	ns	ns	ns	$0.73^{\pounds}$	0.84^{*}	-0.92^{**}	ns
PP-Fe(Fe_{OR})	0.91^{*}	ns	0.89^{*}	0.90^{*}	0.89^{*}	-0.92^{**}	-0.87^{*}
PP-Al	0.84^{*}	ns	ns	$0.78^{\pounds}$	0.87^{*}	-0.93^{**}	$-0.77^{\pounds}$
Fe_{AM}	ns	ns	ns	ns	ns	ns	ns
Fe_{CRY}	0.94^{**}	ns	0.88^{*}	$0.77^{\pounds}$	$0.74^{\pounds}$	$-0.73^{\pounds}$	-0.91^{*}
DC-Fe & Al	0.94^{**}	ns	0.93^{**}	0.83^{*}	$0.79^{\pounds}$	-0.78^{**}	-0.92^{**}
AO-Fe & Al	0.89^{*}	ns	0.88^{*}	0.94^{**}	0.94^{**}	-0.98^{**}	-0.87^{*}
PP-Fe & Al	0.91^{*}	ns	$0.78^{\pounds}$	0.87^{*}	0.91^{*}	-0.96^{**}	-0.85^{*}
ZPNC^{++}	-0.98^{**}	ns	-0.85^{*}	-0.94^{**}	-0.96^{**}	0.93^{**}	0.92^{**}

\+ DC-extracted with dithionite citrate;
AO-extracted with ammonium oxalate;
PP-extracted with sodium pyrophosphate.
Fe_{AM} -difference between AO-Fe and PP-Fe, i.e., amorphous Fe;
Fe_{CRY}-difference between DC-Fe and AO-Fe, i.e., crystalline Fe;
++ Values for non autoclaved soils were used;
1) -Zn without added Zn, +Zn with added Zn (10 mmole kg_{-1});
2) -PP without added PP, +PP with added PP (90 mmole P kg_{-1});
ns not significant; £ significant at $p<0.10$;
* significant at $p<0.05$; ** significant at $p<0.01$;

Table 5. Effects of initial pyrophosphate (PP) and Zn addition rates on Zn fractions and specific Zn sorption.

Initial rate		Zn fraction				Zn_{S3}	Specifically sorbed Zn^+
P	Zn	Zn_{KNO3}	Zn_{NaOH}	Zn_{HNO3}	Sum		
		mmole kg^{-1} soil					
		Uplands topsoil (UT)					
0	0	0.00	0.01	0.13	0.14	-	-
90	0	0.00	0.01	0.38	0.38	-	-
0	10	2.04	1.83	2.82	6.69	6.76	4.72
90	10	1.15	4.50	3.20	8.85	8.52	7.37
$LSD_{0.05}$		0.20	0.03	0.16	0.25	0.23^+	0.56^+
		Uplands subsoil (US)					
0	0	0.00	0.00	0.32	0.32	-	-
90	0	0.00	0.00	0.25	0.25	-	-
0	10	1.49	1.89	2.11	5.49	4.57	3.06
90	10	1.57	3.81	3.02	8.40	7.83	6.26
$LSD_{0.05}$		0.12	0.27	0.18	0.45	0.15	0.42
		St.Bernard topsoil (ST)					
0	0	0.00	0.00	1.01	1.01	-	-
90	0	0.00	0.00	1.02	1.02	-	-
0	10	2.11	1.81	4.68	8.59	7.74	5.63
90	10	0.87	3.57	5.51	9.95	8.80	7.93
$LSD_{0.05}$		0.11	0.07	0.25	0.25	0.27	0.03
		St.Bernard subsoil (SS)					
0	0	0.00	0.00	0.95	0.95	-	-
90	0	0.00	0.00	0.88	0.88	-	-
0	10	2.78	1.14	3.99	7.91	7.28	4.50
90	10	0.96	3.59	5.29	9.83	8.80	7.84
$LSD_{0.05}$		0.01	0.04	0.17	0.20	0.17	0.16
		Dalhousie topsoil (DT)					
0	0	0.00	0.01	1.68	1.69	-	-
90	0	0.00	0.02	1.78	1.80	-	-
0	10	0.75	3.52	6.95	11.22	9.28	8.53
90	10	0.41	4.10	7.27	11.78	9.71	9.30
$LSD_{0.05}$		0.01	0.73	0.38	0.48	ns	0.59
		Dalhousie subsoil (DS)					
0	0	0.00	0.01	1.74	1.75	-	-
90	0	0.00	0.01	1.71	1.72	-	-
0	10	0.82	2.82	7.05	10.69	9.08	8.26
90	10	0.46	3.54	7.41	11.42	9.53	9.07
$LSD_{0.05}$		0.07	0.12	0.15	0.11	ns	0.49

+ LSD value only for locating difference between two means of a soil in columns Zn_{S3} or $Zn_{S3}-Zn_{KNO3}$.

Table 6. Linear correlation coefficients (r) between Zn fractions and properties of autoclaved soils receiving 10 mmole Zn kg^{-1}.

Parameter+	Zn_{KNO3}		Zn_{NaOH}		Zn_{HNO3}	
	-PP1)	+PP2)	-PP	+PP	-PP	+PP
	r					
Clay++	ns	-0.90^{*}	$0.76^{£}$	ns	0.96^{**}	0.94^{**}
CEC	ns	-0.95^{**}	0.83^{*}	ns	0.99^{**}	0.96^{**}
Organic C	ns	-0.94^{**}	$0.77^{£}$	ns	0.97^{**}	0.96^{**}
DC-Fe	ns	-0.82^{*}	ns	ns	0.83^{*}	0.91^{**}
DC-Al	$-0.77^{£}$	-0.96^{**}	0.89^{*}	ns	0.97^{**}	0.93^{**}
AO-Fe	ns	$-0.75^{£}$	ns	ns	ns	$0.78^{£}$
AO-Al	-0.89^{*}	-0.82^{*}	0.93^{**}	ns	0.87^{*}	$0.77^{£}$
PP-Fe	ns	-0.94^{**}	ns	ns	0.96^{**}	0.97^{**}
PP-Al	$-0.76^{£}$	-0.87^{*}	$0.80^{£}$	ns	0.93^{**}	0.89^{*}
Fe_{AM}	ns	ns	ns	ns	ns	ns
Fe_{CRY}	ns	-0.81^{*}	ns	ns	0.84^{*}	0.92^{**}
ZPNC++	ns	0.97^{**}	ns	ns	-0.95^{**}	-0.96^{**}
DC-Fe & Al	ns	-0.85^{*}	ns	ns	0.87^{*}	0.94^{**}
AO-Fe & Al	ns	-0.97^{**}	$0.74^{£}$	ns	0.99^{**}	0.96^{**}
PP-Fe & Al	ns	-0.94^{**}	$0.74^{£}$	ns	0.98^{**}	0.96^{**}
PP_{S3}	-	-0.92^{**}	-	ns	-	0.98^{**}

\+ DC-extracted with dithionite citrate;
AO-extracted with ammonium oxalate;
PP-extracted with sodium pyrophosphate;
Fe_{AM} - difference between AO-Fe and PP-Fe, i.e., amorphous Fe;
Fe_{CRY}-difference between DC-Fe and AO-Fe, i.e., crystalline Fe;

++ Values for non autoclaved soils were used;

1) -PP without added pyrophosphate (PP);

2) +PP with added PP (90 mmole P kg^{-1});

PP_{S3} -PP remaining sorbed at the third equilibration;

ns not significant; £ significant at $p<0.10$;

* significant at $p<0.05$; ** significant at $p<0.01$.

Table 7. Linear correlation coefficients (r) between Zn_{S3}-Zn_{KNO3} and properties of autoclaved soils.

Parameter⁺	Zn_{S3}-Zn_{KNO3}		PP effect on increasing Zn_{S3}-Zn_{KNO3}
	-PP[1)]	+PP[2)]	
	r		
Clay⁺⁺	0.92**	0.89*	-0.89*
CEC	0.97**	0.94**	-0.94**
Organic C	0.95**	0.94**	-0.89*
DC-Fe	ns	ns	ns
DC-Al	0.97**	0.92*	-0.95**
AO-Fe	ns	ns	ns
AO-Al	0.93**	0.82*	-0.97**
PP-Fe	0.91*	0.91*	-0.83*
PP-Al	0.91*	0.82*	-0.97**
Fe_{AM}	ns	ns	ns
Fe_{CRY}	ns	0.79£	ns
Fe_{CRY}/Fe_{AM}	0.76£	0.79£	ns
$Clay/Fe_{Am}$	0.86*	0.79£	-0.88*

\+ DC-extracted with dithionite citrate;
AO-extracted with ammonium oxalate;
PP-extracted with sodium pyrophosphate;
Fe_{AM} -difference between AO-Fe and PP-Fe, i.e., amorphous Fe;
Fe_{CRY}-difference between DC-Fe and AO-Fe, i.e., crystalline Fe;

++ Values for non autoclaved soils were used;

1) -PP without added pyrophosphate (PP);

2) +PP with added PP (90 mmole P kg^{-1});

ns not significant; £ significant at $p<0.10$;

* significant at $p<0.05$; ** significant at $p<0.01$.

Fig. 1. Effect of sorbed Zn (Zn_{S2}) at the second equilibration on Zn desorption (Zn_{D3}) at the third equilibration in the Uplands soils. Lines are calculated values based on regression equations of:

Soil	PP rate (mmole P kg^{-1})		R^2
UT	0	$Zn_{D3} = 0.0162\ Zn_{S2} + 0.0102\ (Zn_{S2})^2$	0.998^{**}
	90	$Zn_{D3} = 0.0199\ Zn_{S2} + 0.0034\ (Zn_{S2})^2$	0.98^{**}
US	0	$Zn_{D3} = 0.0274\ (Zn_{S2})^2$	0.98^{**}
	90	$Zn_{D3} = 0.0375\ Zn_{S2} + 0.0025\ (Zn_{S2})^2$	0.998^{**}

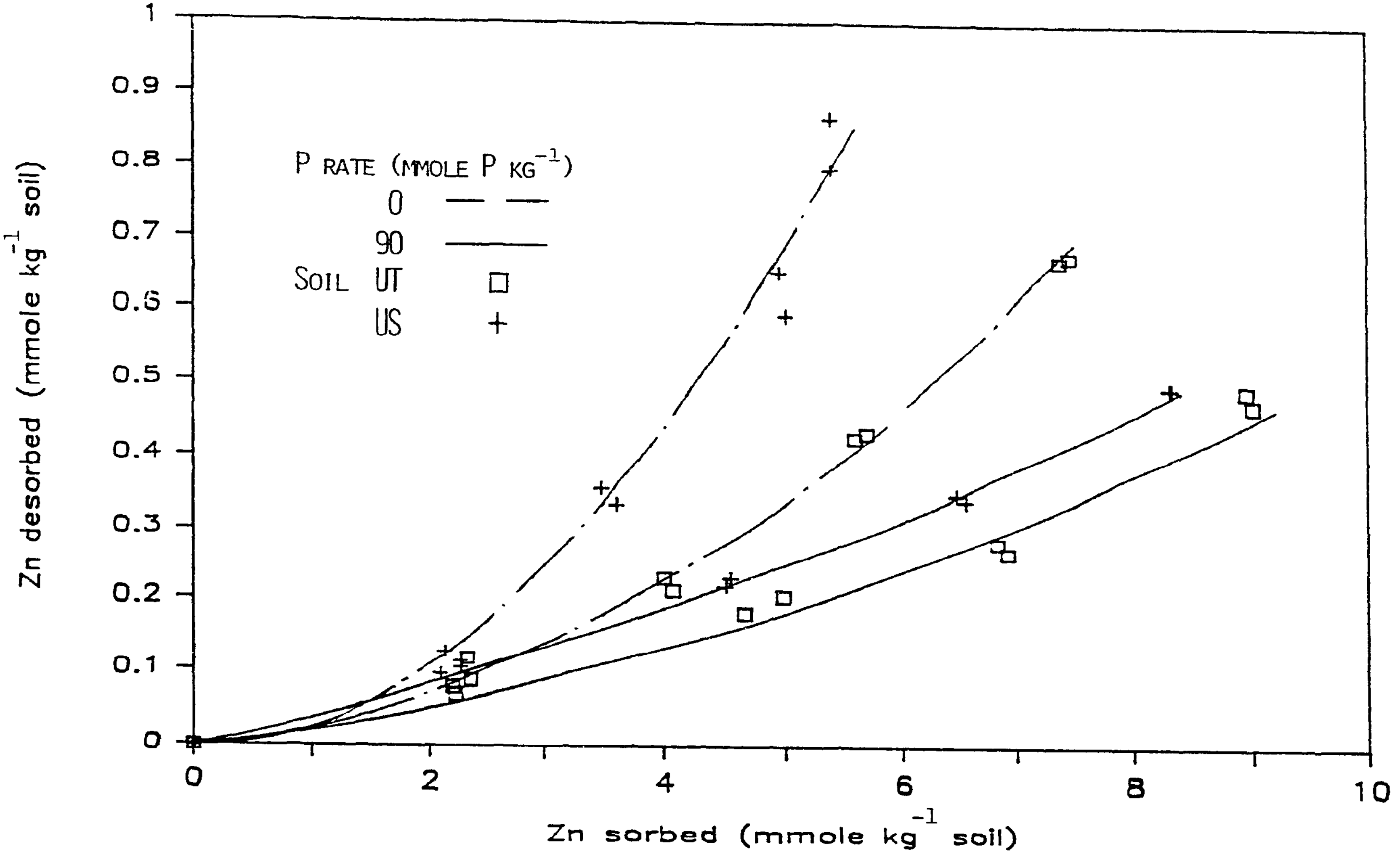

P RATE (MMOLE P KG^{-1})
0
90
SOIL UT
US
Zn desorbed (mmole kg^{-1} soil)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Zn sorbed (mmole kg^{-1} soil)
0
2
4
6
8
10

Fig.2. Effect of sorbed Zn (Zn_{S2}) at the second equilibration on Zn desorption (Zn_{D3}) at the third equilibration in the St.Bernard soils. Lines are calculated values based on regression equations of:

Soil	PP rate (mmole P kg^{-1})		R^2
ST	0	$Zn_{D3} = 0.0336\ Zn_{S2} + 0.0040\ (Zn_{S2})^2$	0.997^{**}
	90	$Zn_{D3} = 0.0168\ Zn_{S2} + 0.0021\ (Zn_{S2})^2$	0.999^{**}
SS	0	$Zn_{D3} = 0.0307\ Zn_{S2} + 0.0067\ (Zn_{S2})^2$	0.998^{**}
	90	$Zn_{D3} = 0.0187\ Zn_{S2} + 0.0018\ (Zn_{S2})^2$	0.997^{**}

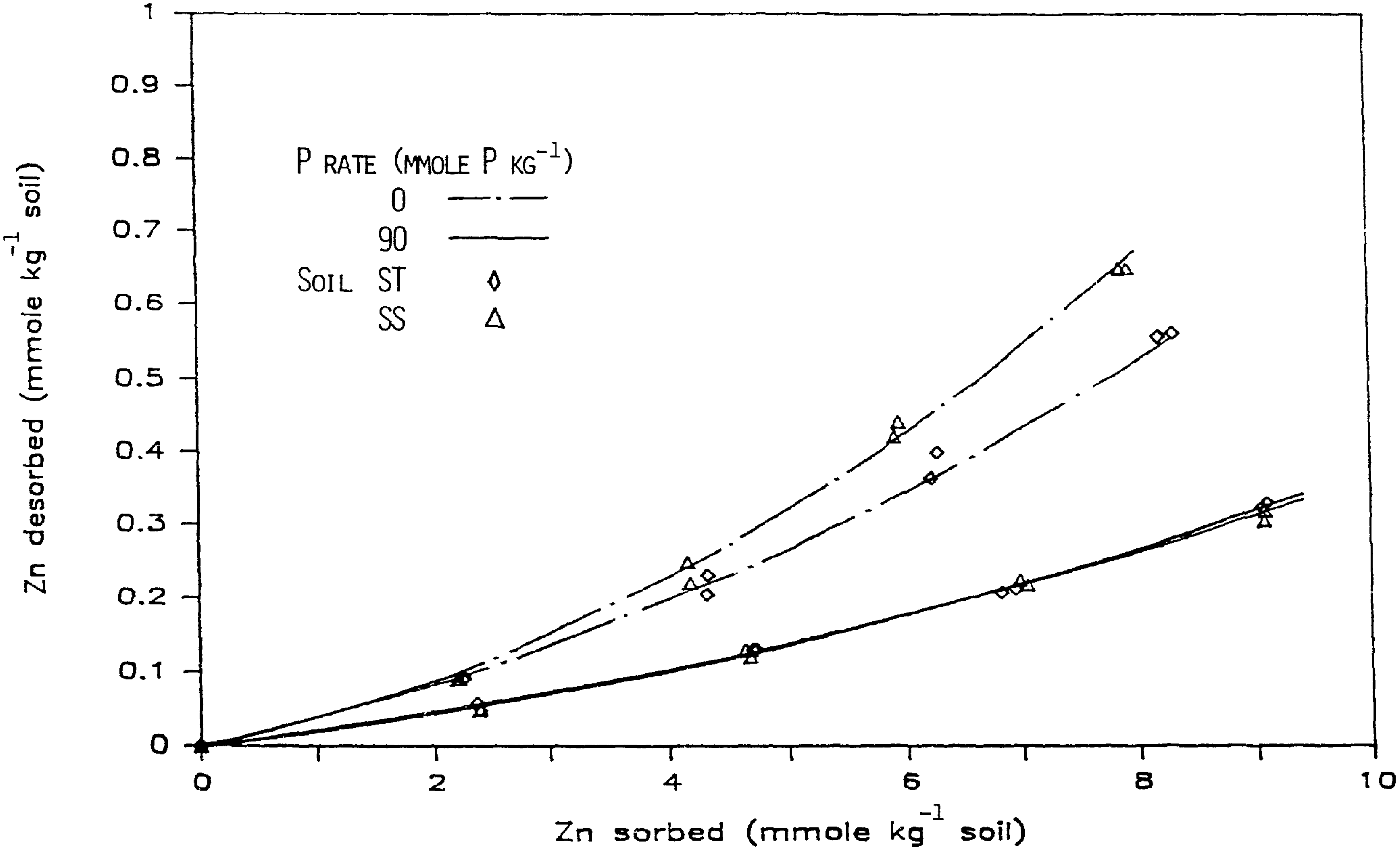
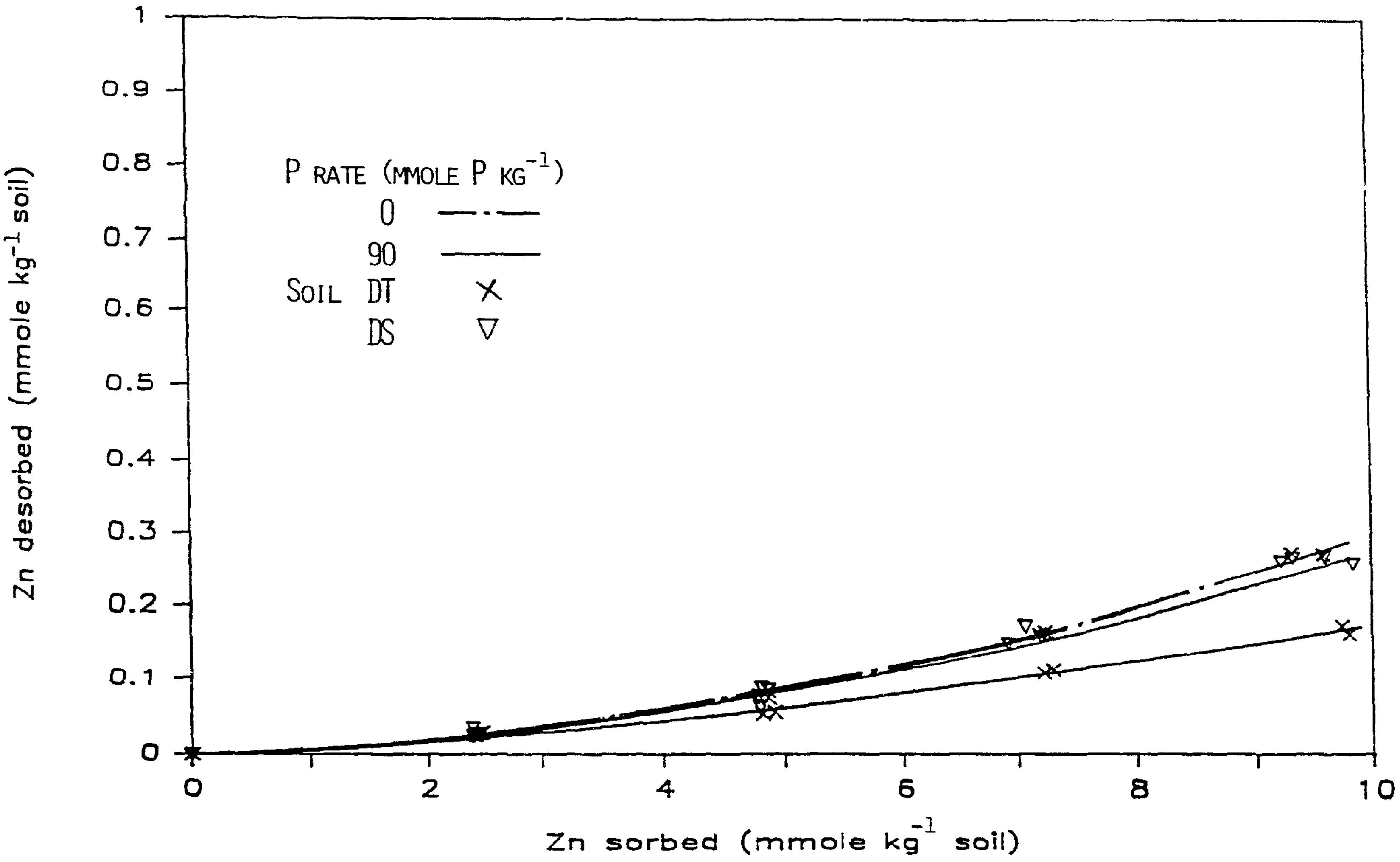

P RATE (MMOLE P KG^{-1})
0
90
SOIL ST
SS
Zn desorbed (mmole kg^{-1} soil)
Zn sorbed (mmole kg^{-1} soil)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
2
4
6
8
10

Fig.3. Effect of sorbed Zn (Zn_{S2}) at the second equilibrationon Zn desorption (Zn_{D3}) at the third equilibration in the Dalhousie soils. Lines are calculated values based on regression equations of:

Soil	PP rate (mmole P kg^{-1})		R^2
DT	0	$Zn_{D3} = 0.0041\ Zn_{S2} + 0.0026\ (Zn_{S2})^2$	0.998^{**}
	90	$Zn_{D3} = 0.0070\ Zn_{S2} + 0.0011\ (Zn_{S2})^2$	0.995^{**}
DS	0	$Zn_{D3} = 0.0059\ Zn_{S2} + 0.0024\ (Zn_{S2})^2$	0.99^{**}
	90	$Zn_{D3} = 0.0057\ Zn_{S2} + 0.0022\ (Zn_{S2})^2$	0.99^{**}


P RATE (MMOLE P KG^{-1})
0
90
SOIL DT
DS
Zn desorbed (mmole kg^{-1} soil)
Zn sorbed (mmole kg^{-1} soil)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10

CONNECTING PARAGRAPH

In Chapter II, orthophosphate (OP) sorption and Zn transformation in non-autoclaved soils was discussed, and it was shown that sorbed OP increased Zn specific sorption. Similar conclusions were also derived in Chapter III with pyrophosphate (PP) in autoclaved soils. It was realized that autoclaving resulted in changes in soil characteristics. For direct comparison of PP with OP, the effect of OP sorption on Zn transformation in autoclaved soils should be evaluated.

In the following Chapter, OP sorption effects on soil CEC, and Zn reactions in autoclaved soils will be examined and compared with PP sorption effects. Comparing the magnitude of the effects of OP-Zn interaction and PP-Zn interaction in soils would help to assess Zn availability to crops grown in soils treated with P fertilizers.

The effect of autoclaving on Zn reactions in soils was assessed in a separate paper but was excluded from this dessertation in order to focus on comparisons of sorbed OP and PP on Zn transformations in soils.

CHAPTER IV

COMPARISONS OF SORBED ORTHO- AND PYROPHOSPHATES ON ZINC REACTIONS IN THREE AUTOCLAVED SOILS

INTRODUCTION

Sorption of ortho- (OP) and pyrophosphate (PP) and the reactions of OP with Zn in soils have been studied extensively. Both OP and PP may increase cation exchange capacity (CEC) of soil (Chapters II and III), form precipitates with Zn in the presence of other ions (Lindsay, 1979; Lehr et al., 1967), induce decreases in solubility of applied Zn (Chapter II and Chapter III), and impose a pH change on localized soil zones, thus affecting Zn solubility (Giordano et al., 1971; Barrow, 1987; Shuman, 1988).

The most frequently cited causes for OP-induced CEC are (1) a shift of surface charge towards more negative values (Hingston et al., 1972), (2) neutralization of positive charges (Hingston et al., 1972), and (3) eletrolyte imbibition (Thomas, 1960). A binuclear surface complex of OP with various Fe and Al oxides has been postulated (Parfitt et al., 1975; Russell et al., 1974) and confirmed by infrared spectroscopic techniques (Martin and Smart, 1987). Such a complex is consistent with an observation of one meq increase in CEC associated with one mmole sorbed P (Chapter II). Each OP replaces two A-type OH or H_2O groups on the surface and two of the oxygen atoms of the P ion are coordinated, each to a different Fe or Al ion (Parfitt et al., 1975; Martin and Smart, 1987), leaving a $-O^-$ bond from the sorbed OP to provide a negative charge, or an OH for subsequent ionization.

Isotherms have been evaluated to describe P sorption behaviour in soils. Amongst the various sorption equations, both OP and PP sorption has been better decribed using the Freundlich isotherm than the Gunary, simple Langmuir, and Temkin equations (Ratkowsky, 1986; Al-kanani, 1985;

Travis and Etnier, 1981). The preferred isotherm for Zn sorption remains to be determined. Mechanisms involved when sorbed PP increases CEC have not been studied to the extent of the OP effects. The increased CEC by both OP and PP, however, was shown not to be the main cause increasing Zn sorption (Chapters II and III).

In contrast, added OP decreases (Al-Showk et al., 1987; Lindsay et al., 1962; Kim et al., 1983; Norvell et al., 1987) while added PP increases (Sheldrick, 1984; Mnkeni and MacKenzie, 1985) solubility of soil Fe and Al, thus possibly influencing Zn solubility (Pulford, 1986). Pyrophosphate has a greater capacity than OP to disperse soil and to dissolve soil organic matter (Mortvedt and Osborn, 1977). This capacity could mobilize micronutrients such as Zn since soluble organic matter forms stable complexes with Zn (Hodgson et al., 1966). Complexed Zn could be less subject to sorption by soil mineral components.

The reported formation constant of the Zn-$P_2O_7^{4-}$ complex ($K=10^8$) is large relative to the formation constant of PP with other cations in soil solution (Wolhoff and Overbeek, 1959). The effectiveness of PP in complexing Zn is dependent on levels of Ca and other metallic cations, solution pH, and initial PP concentration (Asher and Bar-Yosef, 1982; Bar-Yosef and Asher, 1983; Giordano et al., 1971; Mortvedt and Osborn, 1977). Orthophosphate, unlike PP, does not sequester micronutrients such as Zn.

Comparisons were made between effects of PP and of OP on crop P nutrition in field and in greenhouse conditions (Gilliam, 1970; Sutton et al., 1966; Juo and Maduakor, 1973) and on micronutrient availability to plants (Rehm et al., 1980; Schield et al., 1978; Hashimoto and

Wakefield, 1974; Parent et al., 1985). There was little difference shown between PP and OP due to the rapid hydrolysis of PP into OP in soils (Gilliam and Sample, 1968; Savant and Racz, 1972; Dick and Tabatabai, 1986; Tabatabai and Dick, 1979), suggesting that after hydrolysis, PP had similar reactions to OP in the soil. However, delayed hydrolysis of PP was found to reduce P uptake by onions grown in organic soils (Parent et al., 1985)

Under minimized microbial and enzyme activities in autoclaved soils, sorbed PP was found to reduce Zn solubility (Chapter III) as did OP in air-dried soils (Chapter II). Among the effects of increased charge, a P-Zn bridge, sequestering, Zn-P precipitation and specific sorption, the charge effect was discounted in that added P reduced KNO_3-extractable Zn. The bridge effect did not play a significant role while precipitates of hopeite may have existed under limited conditions for OP (Chapters II, III). The effect of solution PP on sequestering Zn was not significant due to the fact that sequestering requires a threshold PP concentration (Bar-Yosef and Asher, 1983), and under soil pH conditions, the $P_2O_7^{4-}$ concentration was expected to be less than 1% of the total PP concentration. Decreased Zn solubility in the soil was mainly a result of increased Zn specific sorption by sorbed P (Chapter II; Chapter III). Comparison of effects of PP and of OP under similar conditions is needed to quantify effects of sorbed PP and OP on Zn solubility in soils.

The objective of this study was to quantify or to compare the mechanisms involved in the reactions of sorbed OP and PP with added Zn in autoclaved soils.

MATERIALS AND METHODS

Experimental procedures were those in Chapter III except that OP was used. Only three surface soil samples were used: Uplands (UT), St.Bernard (ST), and Dalhousie (DT). Three sequential equilibria were conducted between soils and solutions, the first equilibration was for P sorption (OP_{S1} for OP, PP_{S1} for PP) and CEC determination, the second for Zn sorption (Zn_{S2}), P desorption (OP_{D2} for OP, PP_{D2} for PP) or remaining sorbed P (OP_{S2} for OP, PP_{S2} for PP), and third for Zn desorption (Zn_{D3}) or remaining sorbed Zn (Zn_{S3}), P further desorption (OP_{D3} for OP, PP_{D3} for PP) or remaining sorbed P (OP_{S3} for OP; PP_{S3} for PP). Fractions of Zn extracted with 0.5 M KNO_3 (Zn_{KNO3}), 0.5 N NaOH (Zn_{NaOH}) and concentrated HNO_3+30%H_2O_2 (Zn_{HNO3}) represented exchangeable-, organic- and Fe or Al-bonded-, and residual-Zn, respectively. Some comparisons of OP to PP involved results from Chapter III. Isotherms of Freundlich, Gunary, Langmuir, and Temkin were used to evaluate Zn sorption behaviour in soils treated with OP or PP. The equations are expressed as follows:

Freundlich equation, $$\ln(S_{Zn}) = k_1 + k_2 \ln(C_{Zn}) \qquad (1)$$

Gunary equation, $$\frac{C_{Zn}}{S_{Zn}} = k_1 + k_2 C_{Zn} + k_3 (C_{Zn})^{1/2} \qquad (2)$$

Langmuir equation, $$\frac{C_{Zn}}{S_{Zn}} = \frac{1}{K\,S_{ZnM}} + \frac{C_{Zn}}{S_{ZnM}}$$

$$= k_1 + k_2 C_{Zn} \qquad (3)$$

and Temkin equation, $$S_{Zn} = k_1 + k_2 \ln(C_{Zn}) \qquad (4)$$

where S_{Zn} was Zn sorbed per unit of soil (mmole kg^{-1}), C_{Zn} was Zn concentration in solution (mM), S_{ZnM} was Zn sorption maxima, and K a constant for the Langmuir equation. The values of k_1, k_2 and k_3, were determined using multiple regression (Steel and Torrie, 1980). The terms k_1 and k_2 do not have the same meaning in the different equations, but were used to prevent a proliferation of unnecessary terms.

RESULTS AND DISCUSSION

Both sorbed OP and PP increased CEC linearly in the autoclaved soils (Table 1). For OP, one mmole sorbed P resulted in increases in CEC of 0.92 to 1.24 mmole(+), which was greater than values for sorbed PP, which varied from 0.52 to 0.83 mmole(+) $mmole^{-1}$ sorbed P. This implies fewer charges per atom sorbed P as PP than as OP. Increased CEC per unit sorbed P was greater in the finer than in coarser textured soils, which was associated with relatively less amorphous materials in the finer textured soils (Chapter III). Sorption of P as PP was greater than as OP (Table 2) probably due to more active bonds for a PP molecule. Thus absolute increases in CEC (Δ_{CEC}) were greater for added PP than for added OP.

One mmole sorbed OP should result in one mmole(+) increase in CEC assuming a binuclear complex theory (Parfitt et al., 1975; Martin and Smart, 1987) and one negative charge per molecule OP. Values lower than one mmole(+) could be due to precipitated OP (Kim et al., 1983; Lindsay, 1979), overlapping of sorbed OP, unionized OP, or migration of OP into the solid portion (Barrow, 1983; Willett et al., 1988). Thus Δ_{CEC} less than one mmole(+) $mmole^{-1}$ P was an indication of one or more of these processes. Values of Δ_{CEC} greater than one in the DT soil indicate that the binuclear reaction may not have occurred, in that sorbed OP molecule would only use one OH group in coordinating with the sorbent (Barrow and Bowden, 1987). This occurred in the DT soil, suggesting that a binuclear complex may be restricted by soils higher in organic matter or clay, or that OP complexed with single carboxyl or hydroxyl groups in organic molecules.

The configuration of PP (Corbridge, 1974; 1985) indicates that a maximum of four oxygens of PP could react with a "flat" surface of the sorbent, assuming similar binuclear surface complexing per P atom as for OP. Calculations using the geometry data of crystalline oxide materials (Dixon and Weed, 1977; Parfitt et al., 1975) and of PP (Corbridge, 1974; 1985) indicate that it is less likely for the sorbent surface to have four reacting sites accommodating four oxygens of a single PP ion. As well, rotation of the two P atoms around the O atom, i.e., P-O-P (Corbridge, 1985), may result in less than four groups coordinating with the sorbent surface. Thus, with six OH or O groups available (assuming sp hybridization of P-O bonds) for each PP molecule, less than four oxygens of the hydroxyl groups could coordinate with adjacent Fe or Al ions of the sorbent, with the remaining OH or O acting as exchange sites. Thus with this mechanism, for each mmole of PP sorbed (i.e., 2 mmole P) to less than four surface sites, there would be an increase of less than four mmole(+) in CEC, assuming one site consumed one valence, otherwise PP sorption would be less stable. Values less than two (Table 1) would imply some PP sorption using more than two surface sites or more than two O or OH bonds per sorbed PP molecule. Complexes or precipitates of PP with other soil components such as Ca and Fe (Lindsay, 1979) could also reduce CEC increases. The reduced change in

CEC with sorbed PP compared with OP was consistent with sorption through combinations of two, three or four bond coordinations per PP molecule, or with some sorbed PP not being ionized (Fig. 1).

Phosphate sorption increased Zn sorption, especially at high Zn addition rates, and increased Zn sorption was greater with PP than with OP in the coarser textured soil (Table 2; Figs. 2-4), due to more P sorption with PP than with OP or more potential bonds per atom P as PP than as OP. Zinc sorption isotherm regressions indicated that the results fit the Freundlich equation better than with Gunary, Langmuir or Temkin isotherms based on R^2 and cv values (Table 3). Assumptions of one-layer sorption and consistant sorption energy made for Langmuir, Gunary and Temkin isotherms may have limited their applications. The Freundlich equation is an empirical isotherm and is consistent with bonding energy decreases as the fraction of surface covered increases (Travis and Etnier, 1981; Sibbesen, 1981). At the same level of Zn solution concentration, PP increased Zn_{S2} more in the UT, about equal (to) in the ST, and less in the DT soil than OP, compared to zero P (Figs. 2-4).

It has been shown (Chapter II, III) that increased Zn sorption did not result from the coulombic effect since the KNO_3 extractable Zn was reduced with sorbed OP in air-dried soils and with sorbed PP in autoclaved soils. Compared to zero P, added OP did not affect Zn_{KNO3} in the autoclaved UT and ST soils but reduced it in the DT soil, as did PP in all three soils (Table 4). Comparisons between OP and PP showed that Zn_{KNO3} with PP was half of that with OP in the UT and ST soils, indicating that PP was more effective in reducing the portion of coulombically sorbed Zn than OP.

Precipitates of hopeite for OP, and of Fe-Zn, Fe-P-Zn, ZnO or $ZnCO_3$ for both OP and PP may exist in soil systems (Lindsay, 1979; Gupta et al., 1987). Calculations showed that solubility products were below the value of $10^{3.8}$ for hopeite, indicating that hopeite did not form in autoclaved soils treated with OP in contrast to some instances in non-autoclaved soils (Chapter II). For OP, the dissolution of Fe or Al components was not detectable. For PP, dissolved Fe or Al were removed at the first equilibration (unpublished data), with the remaining Fe and Al being well below the concentration required for Fe- or Al-Zn precipitates (Lindsay, 1979). Precipitates of ZnO and $ZnCO_3$ were not possible when pH was below 7.0 and Zn^{2+} concentration below 0.25 mM. Complexes of PP-Zn or organic matter-Zn did not exist or were not significant since Zn sorption was increased with increases in PP addition rates (Table 2).

The increased Zn sorption may have been a result ofa Pbinuclear surface complex with the sorbent, which is subsequently less subject to desorption, creating more active sites (Barrow and Bowden, 1987; Hayes and Leckie, 1987) easily accessed by Zn^{2+} ions.

Calculated ratios of increased Zn sorption to sorbed P (Table 5) were greater with higher P addition rates on the coarser soils. Pyrophosphate tended to produce greater ratios than OP, indicating that part of the sorbed Zn may have formed Zn-P-soil complexes. This effect was most noticeable in the coarser textured soils with higher Zn addition rates, suggesting that the complexation was more likely when a higher proportion of the surface of the sorbent was coated with P. In comparison with models proposed for OP (Stanton and Burger, 1970; Bolland et al., 1977), such complexes could account for increased Zn_{S2} and decreased Zn_{D3} with P additions (Table 2). Relatively, added PP reduced Zn_{D3} more than added OP in the UT soil, about equal in the ST soil, and less in the DT soil. The effect of PP addition on reduction of Zn_{D3} was more significant at high than at low rates of P addition (Table 2).

The complex of P-Zn has been stated to be at the Stern layer or inside the beta plane - an immobile layer (Hayes and Leckie, 1987; Barrow and Bowden, 1987). The energy required to break the bonds of Fe-O, or O-P or O-Zn is extremely high (Bailar, Jr., et al., 1973). In addition, oxygen has an electronegativity of 3.5, and zinc of 1.5. The two atoms can share electron pairs provided by the oxygen. Thus desorption or exchange of such sorbed Zn would be difficult.

Pyrophosphate increased Zn_{NaOH} more than OP, especially in the UT soil (Table 4). The extractant NaOH has been shown to result in dissolution of organic matter and Fe and Al components (Levesque and Schnitzer, 1966). It is plausible to make the induction that since phosphates were mainly sorbed on Fe and Al components (Ballard and Fiskell, 1974; Borggaard, 1983a; 1983b; Mclaughlin et al., 1981; Moody and Radacliffe, 1986), and Zn was complexed with the sorbed P, then when Fe and Al materials were extracted by NaOH, the Zn-P complex would also be dissolved. The Zn_{HNO3} which was strongly bonded with the sorbent material or sorbed P was increased in the presence of sorbed OP and PP, and greater differences between PP and OP were observed in the UT soil.

Both PP and OP increased specific Zn sorption (Zn_{S3}-Zn_{KNO3}), with

PP being more significant than OP (Table 4). The value of increased Zn_{S3}-Zn_{KNO3} for PP over that for OP was highest in the UT and lowest in the DT soil, suggesting that P sorption was more effective in increasing specifc Zn sorption in the coarser textured soil, where PP sorption produced more sorption sites, compared with OP.

CONCLUSIONS

Total increased CEC at a fixed P addition rate was greater with PP than with OP as a result of more P sorption as PP than as OP, due to the possibility of PP having a greater number of bonds per molecule, compared with OP. Increased CEC per atom of sorbed P was greater with sorbed OP than with sorbed PP probably because of sorbed PP molecules having more than two O or OH groups complexing with sorbent surfaces.

The reduced effect of OP on increasing Zn sorption compared with PP could be due to a number of mechanisms. Reduced strength of bonding with OP may have produced a less stable sorbed P complex. On other hand, PP was more effective in dissolution of organic matter or organic matter-Fe or Al complexes than OP, exposing more sites for Zn sorption, so there was more Zn_{NaOH} and Zn_{HNO3} with PP than with OP. Thus specific Zn sorption was increased more with PP than with OP, most significantly in coarser textured soils.

Thus sorbed PP would be expected to result in reduced Zn solubility, at least until hydrolysis. Zinc applications following PP fertilization should be placed out of the zone of PP-soil reactions.

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Table 1. Ortho- (OP) and pyrophosphate (PP) sorption effects on changes in soil cation exchange capacity (Δ_{CEC}).

P form	Soil	Regression Equation	R^2	P
OP	Uplands	$\Delta_{CEC} = 0.92(\pm 0.11)\ OP_{S1}$ +	0.90^{**}	0.0001
OP	St.Bernard	$\Delta_{CEC} = 0.96(\pm 0.19)\ OP_{S1}$	0.76^{**}	0.0011
OP	Dalhousie	$\Delta_{CEC} = 1.24(\pm 0.15)\ OP_{S1}$	0.89^{**}	0.0001
PP++	Uplands	$\Delta_{CEC} = 0.52(\pm 0.06)\ PP_{S1}$	0.91^{**}	0.0001
PP	St.Bernard	$\Delta_{CEC} = 0.70(\pm 0.04)\ PP_{S1}$	0.97^{**}	0.0001
PP	Dalhousie	$\Delta_{CEC} = 0.83(\pm 0.04)\ PP_{S1}$	0.98^{**}	0.0001

\+ ± 95% confidence limit;
OP_{S1}, PP_{S1} = sorbed OP and PP, mmole P kg^{-1} soil;
Δ_{CEC}, mmole(+) kg^{-1};
++ data for PP are from Chapter III;
** significant at $p<0.01$.

Table 2. Phosphate addition effects on sorption (Zn$_{S2}$) and desorption (Zn$_{D3}$) of Zn in autoclaved soils (Zn rate=10 mmole kg^{-1}).

P form	P rate	Sorbed P (OP$_{S1}$, or PP$_{S1}$)	Δ_{CEC}	Zn$_{S2}$	Increased Zn$_{S2}$	Increased Zn$_{S2}$ as a proportion of Δ_{CEC} 1)	$\frac{Zn_{D3}}{Zn_{S2}}$
	---mmole	kg^{-1}---	mmole(+) kg^{-1}	--mmole	kg^{-1}--	------- %	------
				Uplands soil			
-	0	-	-	7.41	-	-	9.04
OP	30	6.7	6.4	7.51	0.10	3.1	7.68
OP	60	10.2	8.6	8.00	0.59	13.7	6.55
OP	90	11.4	11.0	7.96	0.55	10.0	5.82
PP	30	21.1[+]	14.1[1]	8.34	0.93	12.9	6.01
PP	60	31.8	18.7	8.74	1.33	14.2	5.32
PP	90	46.3	21.0	8.98	1.57	14.9	5.37
	LSD$_{0.05}$	-	-	0.08	-	-	0.70
				St.Bernard soil			
-	0	-	-	8.24	-	-	6.11
OP	30	7.6	10.6	8.68	0.44	8.3	4.02
OP	60	10.7	11.4	8.66	0.42	7.4	3.78
OP	90	16.8	16.0	8.83	0.59	7.3	3.65
PP	30	24.0	19.0	8.49	0.25	2.6	4.48
PP	60	45.1	34.8	8.97	0.73	4.2	3.72
PP	90	64.6	41.7	9.07	0.83	4.0	3.04
	LSD$_{0.05}$	-	-	0.11	-	-	0.60
				Dalhousie soil			
-	0	-	-	9.44	-	-	2.89
OP	30	9.3	18.0	9.43	-0.01	-	1.86
OP	60	17.5	22.2	9.37	-0.07	-	1.43
OP	90	24.8	28.5	9.64	0.20	1.4	1.64
PP	30	26.5	22.4	9.49	0.05	0.4	2.21
PP	60	54.4	48.7	9.78	0.34	1.4	2.14
PP	90	80.6	64.5	9.76	0.32	1.0	1.76
	LSD$_{0.05}$	-	-	0.30	-	-	0.36

1) calculated as $(Zn_P-Zn_0)\times2\times100/(\Delta_{CEC})_i$, $Zn_P=Zn_{S2}$ with added OP or PP, $Zn_0=Zn_{S2}$ without added OP or PP, Δ_{CEC}=increased CEC by added OP or PP, i=P rate;

\+ data for PP$_{S1}$ and Δ_{CEC} for PP are from Chapter III.

Table 3. Parameters of Zn sorption isotherms as affected by P addition.

OP or PP addition mmole P kg^{-1}	Sorption isotherms	Parameters			R^2	p-value	cv, %
		k_1	k_2	k_3			
Uplands soil							
NP^+ 0	Freundlich	2.6795	0.5037	-	0.9918	0.0001	3.2
	Gunary	-0.0050^{ns}	-0.0688^{ns}	0.1102	0.9893	0.0001	4.9
	Langmuir	0.0101	0.1016	-	0.9328	0.0001	11.1
	Temkin	9.7914	2.0863	-	0.9351	0.0001	11.7
OP 90	Freundlich	2.9534	0.4335	-	0.9967	0.0001	2.0
	Gunary	0.0002^{ns}	0.0368	0.0326	0.9997	0.0001	1.1
	Langmuir	0.0033	0.1052	-	0.9854	0.0001	7.4
	Temkin	11.4348	1.9198	-	0.9820	0.0001	6.3
PP 90	Freundlich	3.8366	0.6501	-	0.9566	0.0001	7.4
	Gunary	0.0059	0.1187	-0.0215^{ns}	0.9827	0.0001	5.0
	Langmuir	0.0039	0.0674	-	0.9727	0.0001	5.7
	Temkin	16.7036	3.2358	-	0.9958	0.0001	3.2
St.Bernard soil							
NP 0	Freundlich	3.2334	0.6343	-	0.9948	0.0001	2.6
	Gunary	-0.0013^{ns}	-0.0829	0.0853	0.9872	0.0001	3.6
	Langmuir	0.0091	0.0718	-	0.9152	0.0002	8.5
	Temkin	12.7336	2.8201	-	0.9411	0.0001	11.9
OP 90	Freundlich	3.5990	0.5617	-	0.9940	0.0001	2.7
	Gunary	0.0014	0.0302^{ns}	0.0194	0.9968	0.0001	2.6
	Langmuir	0.0030	0.0801	-	0.9879	0.0001	4.7
	Temkin	15.1964	2.7078	-	0.9836	0.0001	6.3
PP 90	Freundlich	4.0643	0.7104	-	0.9948	0.0001	2.6
	Gunary	0.0036	-0.0361^{ns}	0.0074^{ns}	0.9933	0.0003	2.1
	Langmuir	0.0043	0.0550	-	0.9912	0.0003	2.2
	Temkin	17.6868	3.4910	-	0.9812	0.0001	6.9
Dalhousie soil							
NP 0	Freundlich	4.0507	0.6123	-	0.9922	0.0001	3.1
	Gunary	0.0013	0.0279^{ns}	0.0129	0.9942	0.0001	3.0
	Langmuir	0.0022	0.0684	-	0.9869	0.0001	4.2
	Temkin	18.0707	3.1102	-	0.9820	0.0001	6.8
OP 90	Freundlich	4.3211	0.5889	-	0.9978	0.0001	1.7
	Gunary	0.0003^{ns}	0.0021^{ns}	0.0160	0.9959	0.0001	2.7
	Langmuir	0.0012	0.0698	-	0.9744	0.0001	6.2
	Temkin	19.5609	3.0116	-	0.9696	0.0001	9.0
PP 90	Freundlich	4.1766	0.5840	-	0.9678	0.0001	6.3
	Gunary	-0.0000^{ns}	-0.0402^{ns}	0.0277	0.9611	0.0003	7.9
	Langmuir	0.0015	0.0667	-	0.9075	0.0003	11.2
	Temkin	18.9593	3.0188	-	0.9310	0.0001	13.5

+ NP zero added P; ns not significant.

Table 4. Zinc fractions and specific sorption as affected by additions of phosphates (Zn rate = 10 mmole kg^{-1}) in autoclaved soils.

P form+	Zn_{S3}	Zn fractions			Zn_{S3}-Zn_{KNO3}	P effect on increasing Zn_{S3}-Zn_{KNO3} 1)
		Zn_{KNO3}	Zn_{NaOH}	Zn_{HNO3}		
	mmole kg^{-1} soil					
	Uplands soil					
NP	6.76	2.04	1.83	2.82	4.72	-
OP	7.50	2.04	3.27	2.82	5.46	0.74
PP	8.52	1.15	4.50	3.20	7.37	2.65
$LSD_{0.05}$	0.15	0.28	0.22	0.25	0.35	0.59
	St.Bernard soil					
NP	7.74	2.11	1.81	4.68	5.63	-
OP	8.47	1.84	2.77	5.53	6.63	1.00
PP	8.80	0.87	3.57	5.51	7.93	2.30
$LSD_{0.05}$	0.19	0.26	0.15	0.14	0.31	0.52
	Dalhousie soil					
NP	9.28	0.75	3.52	6.95	8.53	-
OP	9.49	0.47	3.66	7.18	9.02	0.49
PP	9.71	0.41	4.10	7.27	9.30	0.77
$LSD_{0.05}$	0.38	0.06	ns	ns	0.37	0.20

\+ NP - with zero added P;
OP - with added orthophosphate (90 mmole P kg^{-1} soil);
PP - with added pyrophosphate (90 mmole P kg^{-1} soil);
values for NP and PP are from Chapter III;

1) values were calculated as $(Zn_{S3}-Zn_{KNO3})_{OP}$ - $(Zn_{S3}-Zn_{KNO3})_{NP}$,
or $(Zn_{S3}-Zn_{KNO3})_{PP}$ - $(Zn_{S3}-Zn_{KNO3})_{NP}$.

Table 5. Effect of P and Zn addition rates on the ratio of sorbed Zn to sorbed P in soils.

P form	P rate	Zn rate, mmole kg^{-1}				$LSD_{0.5}^{+}$
		2.5	5.0	7.5	10.0	
	mmole kg^{-1}					
			Uplands soil			
OP	30	0.044[1)]	0.109	0.114	0.057	0.046
OP	60	0.083	0.223	0.206	0.197	0.085
OP	90	0.065	0.231	0.269	0.203	0.061
PP	30	0.122	0.229	0.324	0.281	0.037
PP	60	0.132	0.293	0.407	0.371	0.042
PP	90	0.092	0.348	0.423	0.414	0.121
$LSD_{0.05}^{++}$		ns	0.087	0.055	0.016	
			St.Bernard soil			
OP	30	0.095	0.106	0.154	0.132	ns
OP	60	0.112	0.171	0.153	0.131	ns
OP	90	0.140	0.204	0.239	0.182	0.061
PP	30	0.098	0.093	0.139	0.087	0.036
PP	60	0.137	0.130	0.220	0.205	0.020
PP	90	0.148	0.205	0.243	0.241	0.040
$LSD_{0.05}^{++}$		ns	0.049	0.073	0.026	
			Dalhousie soil			
OP	30	0.020	-0.040	-0.000	0.018	ns
OP	60	0.004	-0.055	0.008	0.014	ns
OP	90	0.020	0.006	0.039	0.066	0.035
PP	30	-0.023	-0.045	-0.011	0.023	ns
PP	60	0.032	0.044	0.042	0.083	ns
PP	90	0.041	0.011	0.032	0.098	0.049
$LSD_{0.05}^{++}$		ns	ns	ns	0.063	

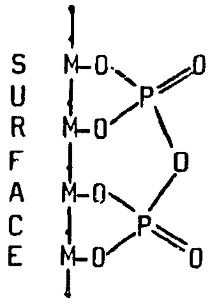
\+ for locating significant difference between means in the row - the effect of Zn rate;

++ for locating significant difference between means in a column under a soil - the effect P forms and rates;

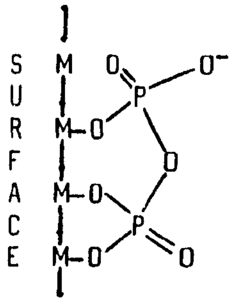
1) values were calculates using the formular of ratio = $((Zn_{S3})_i - (Zn_{S3})_o) / (0.5 \times P_{S3})$, where Zn_{S3} = sorbed Zn (mmole kg^{-1} soil) at the third equilibration, i = Zn rate, o = zero added Zn, P_{S3} = sorbed OP or PP (mmole P kg^{-1} soil);

ns not significant at the level 0.05.

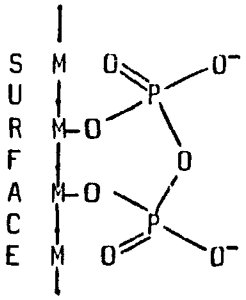
Fig. 1. Schematic representation of PP sorption on surface of soil particles, where M=Fe, Al. (i) sorption with four bonds, no incease in CEC; (ii) sorption with three bonds, 0.5 mmole(+) increase in CEC per atom P; (iii) sorption with two bonds from two P atoms, 1.0 mmole(+) increase in CEC; (iv) sorption with two bonds from one P atom, 1.0 mmole(+) increase in CEC; (v) sorption with one bond, 1.5 mmole(+) increase in CEC; (vi) sorption with two bonds from two P atoms, sorbed P not ionized and no increase in CEC.



(i)



(ii)



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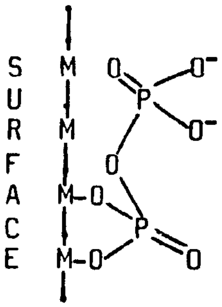

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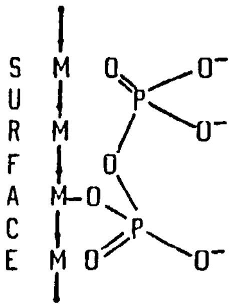

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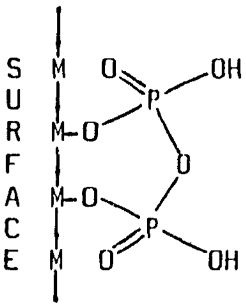


(vi)

Fig. 2. Zinc sorption isotherms in autoclaved Uplands soil treated with ortho- or pyrophosphates. Lines are the calculated values based on the Freundlich sorption isotherms (Table 3).

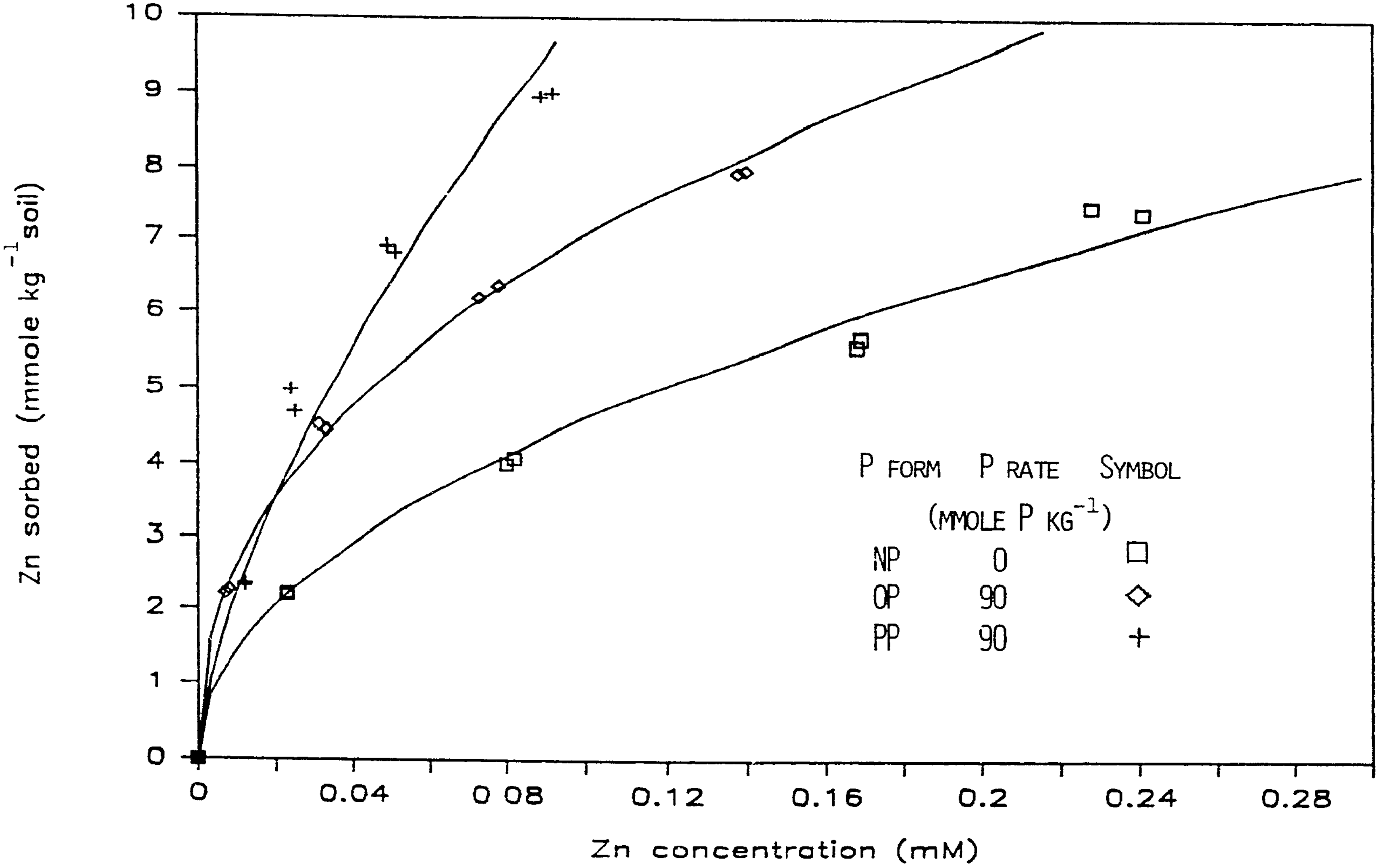
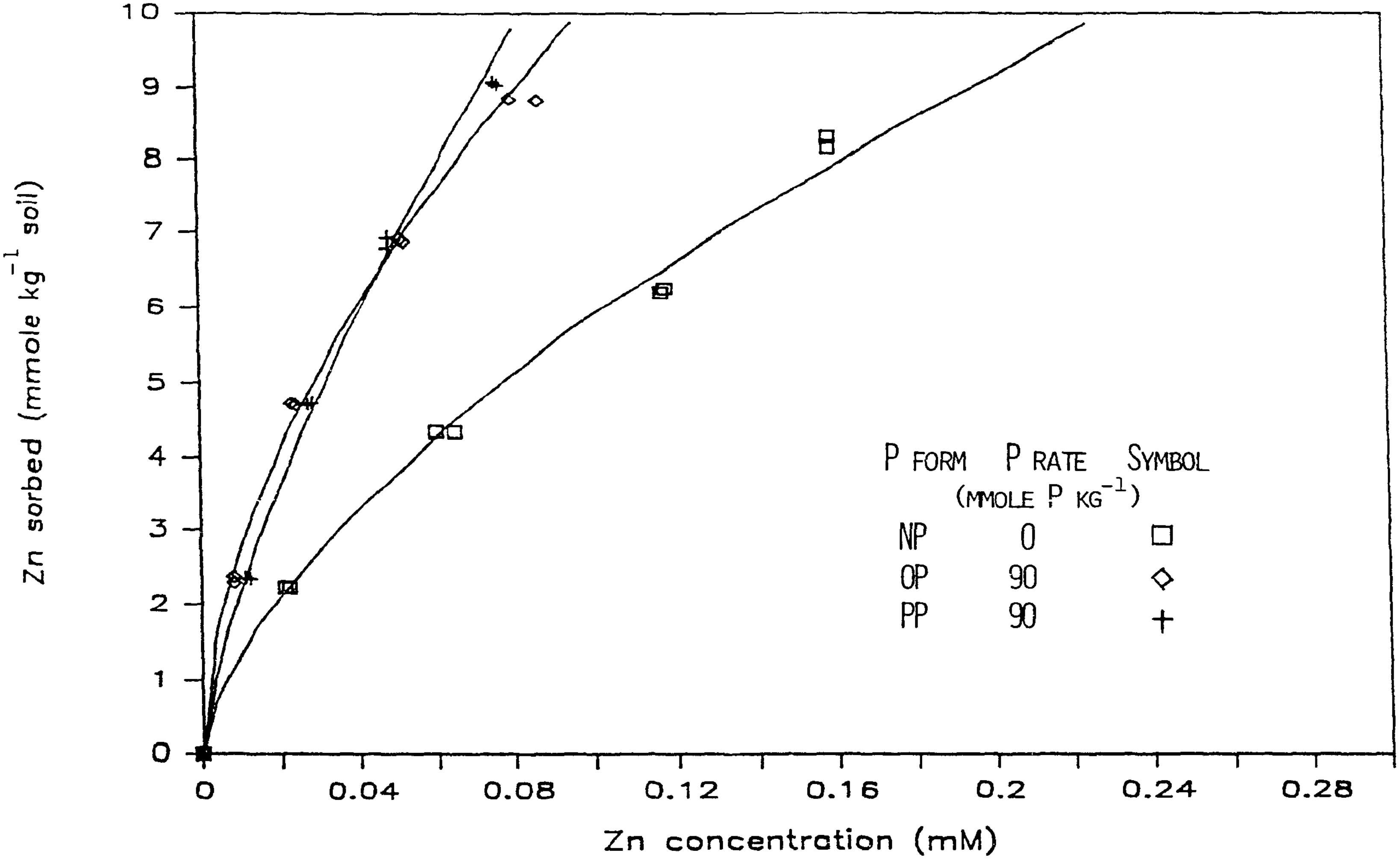
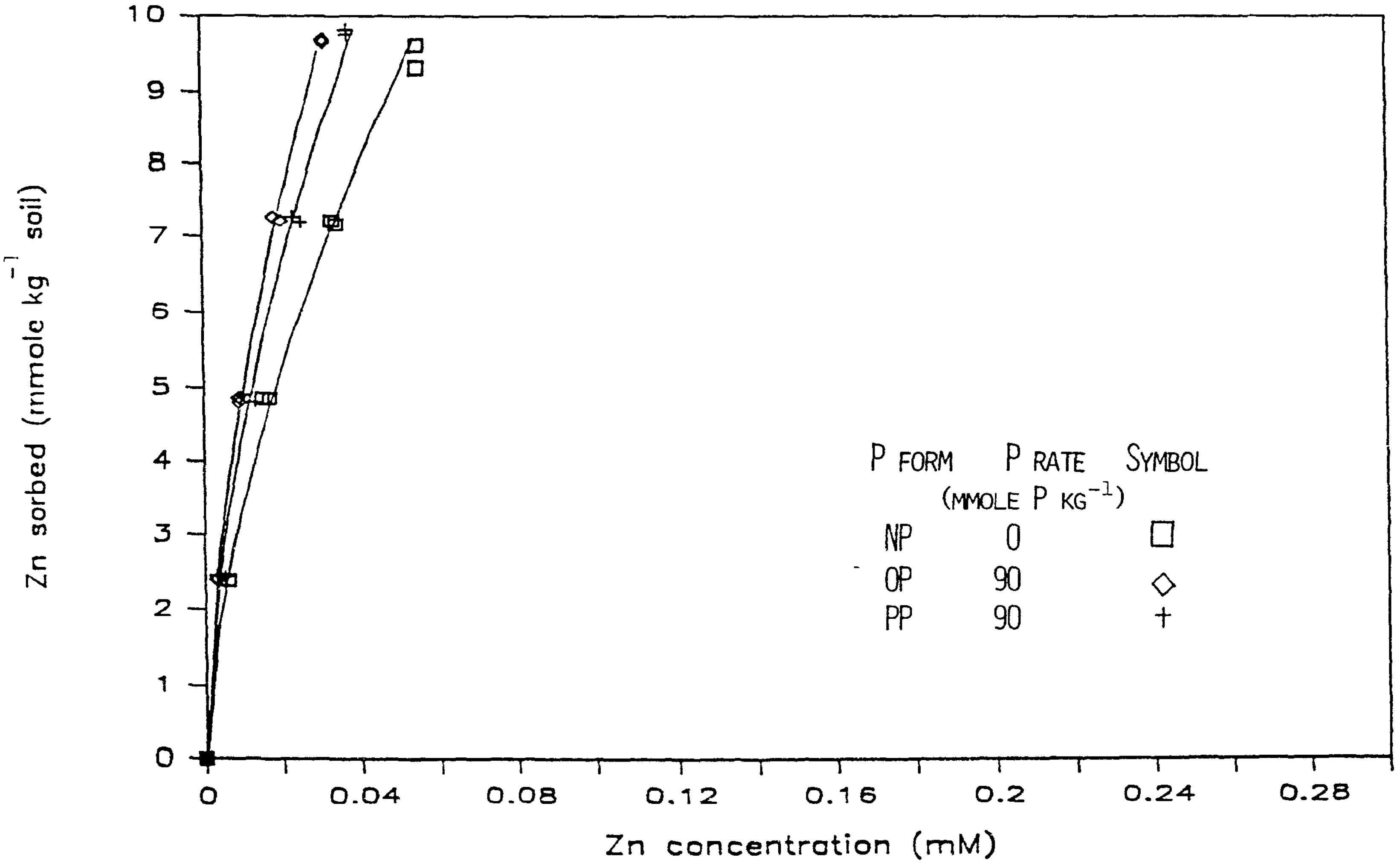

Zn sorbed (mmole kg^{-1} soil)
0
1
2
3
4
5
6
7
8
9
10
0
0.04
0 08
0.12
0.16
0.2
0.24
0.28
Zn concentration (mM)
P FORM
P RATE
SYMBOL
(MMOLE P KG^{-1})
NP
0
□
OP
90
◇
PP
90
+

Fig. 3. Zinc sorption isotherms in autoclaved St.Bernard soil treated with ortho- or pyrophosphates. Lines are the calculated values based on the Freundlich sorption isotherms (Table 3).

Fig. 4. Zinc sorption isotherms in autoclaved Dalhousie soil treated with ortho- or pyrophosphates. Lines are the calculated values based on the Freundlich sorption isotherms (Table 3).


Zn sorbed (mmole kg^{-1} soil)
0
1
2
3
4
5
6
7
8
9
10
0
0.04
0.08
0.12
0.16
0.2
0.24
0.28
Zn concentration (mM)
P FORM
P RATE (MMOLE P KG^{-1})
SYMBOL
NP 0 □
OP 90 ◇
PP 90 +


10
9
8
7
6
5
4
3
2
1
0
Zn sorbed (mmole kg^{-1} soil)
0
0.04
0.08
0.12
0.16
0.2
0.24
0.28
Zn concentration (mM)
P FORM
P RATE (MMOLE P KG^{-1})
SYMBOL
NP 0 □
OP 90 ◇
PP 90 +

GENERAL CONCLUSIONS AND FUTURE RESEARCH

Zinc solubility has been reported to be increased by pyrophosphate (PP) addition (Mortvedt and Osborn, 1977; Bar-Yosef and Asher, 1983), which is in contrast to observations that crop Zn nutrition was not improved by PP application. Hydrolysis of PP to orthophosphate (OP) (Parent and MacKenzie, 1985; Dick and Tabatabai, 1986) has limited studies comparing effects of the two P sources on Zn reaction in soils. Autoclaving provided a delay in PP hydrolysis (Tabatabai and Dick, 1979) and allowed studies of PP and OP under comparable conditions.

Autoclaving resulted in changes in soil properties, particularly in Al and Fe materials. Extractable Al was reduced by autoclaving. When extractable Fe was partitioned into organic (Fe_{OR}), amorphous (Fe_{AM}), and crystalline Fe (Fe_{CRY}), it was shown that autoclaving reduced Fe_{OR} and the ratio of Fe_{CRY}/Fe_{AM} while Fe_{AM} was not affected. Subsequently, autoclaving reduced cation exchange capacity (CEC) of the Uplands top- (UT) and sub-soils (US) while it increased CEC of St.Bernard top- (ST) and sub- (SS), Dalhousie top- (DT) and sub-soils (DS). Autoclaving decreased OP sorption in all soils, possibly due to hastening of the process of converting Fe_{OR} to more crystallized materials. Comparing effects of PP in autoclaved soils with OP in non-autoclaved was not appropriate due to such changes.

Pyrophosphate sorption resulted in increases in soil CEC as did OP. Comparisons between PP and OP in autoclaved soils indicated that in terms of per atom of sorbed P, CEC was increased less with PP than with OP. A sorbed PP molecule, having less than four bonds (valence) coordinating with the sorbent, would leave the remaining bonds (valence) displaying negative charges per two P atoms. With OP, two bonds (valence) coordinating with the sorbent would leave one bond (valence) displaying charge per P atom.

The absolute increase in CEC was greater for PP than for OP at a fixed rate of P addition (mmole P kg^{-1} soil), because of more P sorption as PP than as OP in autoclaved soils. Greater sorption was probably due to greater numbers of bonds available for a molecule of PP than for a molecule of OP. This could be important in soil management or fertilization practice, especially for soils with low base saturation or low levels of crop nutrients, where OP and PP application may enhance sorption of nutrients (cations), which would otherwise be subject to leaching. On the other hand, in fine textured soils, application of P may further reduce solubility of cation nutrients, such as Zn, through enhanced sorption. However, at normal rates of P application, such effects should not be overestimated.

Sorbed PP increased soil capacities for Zn sorption more than sorbed OP, probably due to more active linkages of PP with soil surfaces, thus creating a more stable impact of sorbed PP on added Zn. This PP-induced Zn sorption was more significant in coarser textured soils of lower organic matter than in finer textured soils of higher organic matter levels. The amount of Zn desorption was a quadratic function of the amount of Zn sorbed, indicating that energy of Zn desorption was not equal across all levels among sorbed Zn. Sorbed PP and OP may have raised the energy level needed for Zn desorption, thus reducing Zn desorption.

Sorbed PP resulted in increases in specific Zn sorption in autoclaved soils as did OP in both autoclaved and non-autoclaved soils. More specific Zn sorption with PP may have been due to PP exposing more sites for Zn sorption. These sites were probably occupied by organic matter or organic matter-Fe or Al materials. Interaction of PP-Zn or OP-Zn was effective in coarser than in finer textured soils. Observations indicated that the association between the decrease in soluble Zn and the increase in surface negative charge or CEC by P addition (Saeed and Fox, 1979) was not a related phenomenom, and PP increased specific Zn sorption more than OP, particularly in coarser textured soils.

A precipitate, hopeite ($Zn_3(PO_4)_2.4H_2O$), may have formed in some treatments of non-autoclaved soils with OP, since the calculated solubility products (K_{SP}) exceeded the value of $10^{3.8}$ (K_{SP} for hopeite) in some instances. In autoclaved soils, there was no evidence of hopeite.

The effect of P addition either as OP or as PP on native Zn dissolution and fraction transformation in the soil was not significant.

The interactions between OP and Zn in non-autoclaved soils or PP and Znin autoclaved soils occurred mainly in association with Fe or Al components as indicated by increased or decreased correlations between Zn (or P) parameters (sorption, desorption, and fractions) and Fe or Al fractions, suggesting that there existed P-Zn-Fe or Al complexes and that P application was most likely to induce crop Zn deficiency insoils rich in Fe or Al materials.

The ratio of increased Zn sorption to sorbed P increased with higher rates of P addition, and coarser soil textures, indicating that the specific Zn sorption was more likely in soils with a higher than with a lower fraction of surface coverage by sorbed P, and with PP than with OP. Higher organic matter contents may reduce the probabilities of forming specific sorption sites.

The practical implication of the above findings is that if Zn addition is recommonded following OP or PP application, Zn should be placed out of the zone of P reaction, in order to maintain a certain level of Zn in solution for crop utilization.

Significant findings have been made in this research. However, work should be continued to confirm or complete the following.

1. A confirmation of number of bonds involvedin reactions between PP and soil components is necessary. Procedures of Martin and Smart (1987) -- X-ray photoelectron or of Willett et al. (1988) -- infra-red spectrometry, using pure crystalline Fe or Al materials as well as soil samples. Procedures to apply these techniques to a whole soil sample need to be developed. Such studies would provide a theoretical basis for determining PP surface reactions with sorbents. Simultaneously, a measurement of surface area might be done to determine sorbed P and surface area effects.
2. An investigation of changes in CEC of mixtures of crystalline and amorphous Fe or Al materials with added OP and PP could be carried out to examine whether the relative precipitated P compounds contribute to increases in CEC.
3. Structures of OP or PP and Zn complexes on particle surfaces

need to be verified, perhaps using X-ray photoelectron techniques (Martin and Smart, 1987). This could be done with pure crystalline Fe and Al materials and treated natural soil materials.

4. A desorption study in combination with the above may be required to evaluate the bonding energy of the OP or PP and Zn on soil particle surfaces. This would indicate to what extent bound Zn would be available to plants.

5. A hydroponic study should be established using pure crystalline Fe or Al or clay minerals coated with either OP or PP, following a technique similar to that of Tjepkema et al. (1981). A range of Zn addition rates would be assessed to examine the availability of the sorbed Zn to plants. Solutions of OP and Zn or PP and Zn could be used to test whether P sorption would affect Zn absorption by the plant and Zn translocation in the plant.

6. Pot experiments, using soils of various characteristics, could be initiated to determined effects of different P sources (OP and PP) and Zn application methods or sequences on crop Zn nutrition. Treatments could include band application of P and Zn together, or separately, and rates and residual effect could be evaluated and quantified.

Subsequently, various management approaches could be practiced to increase desorption of specifically bound Zn, increasing Zn availability to plants.

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Appendix I

Specific conductivity of suspension of soil-phosphate after the first equilibration.

P concentration in 0.03 M $KClO_4$	Solution of P	Soil					
		UT	US	ST	SS	DT	DS
P mM L^{-1}	mS cm^{-1}						
		Orthophosphate (OP)					
0.00	3.34	4.21	4.16	4.42	4.27	3.99	4.12
1.20	3.44	3.56	3.95	3.68	4.10	3.76	4.19
3.00	3.65	4.58	4.11	3.64	4.10	3.63	4.28
6.00	4.03	4.64	4.22	4.25	4.25	4.55	4.22
9.00	4.43	4.65	4.50	4.35	4.31	4.60	4.26
$LSD_{0.05}$	-	1.02	0.25	0.74	ns	ns	ns
		Pyrophosphate (PP)					
0.00	3.34	3.97	3.64	3.75	3.64	3.64	3.60
1.20	3.51	3.98	3.89	3.82	3.71	3.63	3.40
3.00	3.86	4.22	4.01	3.97	3.92	3.91	3.98
6.00	4.35	4.29	4.34	4.30	4.18	4.06	4.12
9.00	4.71	4.69	4.94	4.84	4.43	4.33	4.45
$LSD_{0.05}$	-	0.21	0.11	0.24	0.44	0.17	0.48

ns -not significant at $p < 0.05$.

Appendix II

Manuscript of Xie and MacKenzie (1988) in Commun.
Soil Sci. Plant Anal., 19: 873-886.

THE pH EFFECT ON SORPTION-DESORPTION AND FRACTIONS OF ZINC IN PHOSPHATE TREATED SOILS

Key Words: pH, buffer, Zn sorption, Zn desorption, Zn fractions.

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ABSTRACT

Zinc sorption-desorption and Zn fractions in three soils, a Dalhousie clay (DT: Typic Haplorthod), a St. Bernard loam (ST: Typical Eutrochrept) and an Uplands sand (UT: Typical Humaquept), were studied with and without added P at different pH values. Phosphate addition increased Zn sorption (Zn_S) in the order: DT clay > ST loam > UT sand. A positive correlation was noted between Zn_S and pH for soils treated with and without P. Phosphate addition reduced Zn desorption (Zn_D) especially at low pH and was attributed to P induced pH effect. At high pH values, the P effect was less important. An increase in pH value resulted in less 0.5 M KNO_3-extractable Zn (Zn_{KNO3}) and more 0.5 NaOH-Zn (Zn_{NaOH}) and HNO_3 extractable Zn (Zn_{HNO3}). Compared with zero P treatments, P addition reduced Zn_{KNO3} at low pH value but increased Zn_{NaOH} at all pH values.

INTRODUCTION

Of the factors affecting soil Zn availability to plants, pH and P have been subjected to intensive studies[1,2]. The pH-dependent surface charge tends to shift to less negative values at lower pH resulting in less Zn sorption[3]. Increases in P sorption on particle surfaces at constant pH may enhance Zn sorption through increases in negative charge on surfaces[4], thus reducing Zn solubility. Stanton and Burger[5] believed that the sorbed P acted as a "bridge" between surface and sorbed Zn while Pasricha et al.[6] showed that applying P to soils did not decrease Zn concentrations in the soil solutions. Barrow[2] recently reported that the effect of P on Zn sorption included a P-induced pH effect which either increased or decreased $ZnOH^+$ species, thus influencing Zn sorption. Parfitt[7] noted an increase in pH with added P, which would decrease Zn in solution.

In a previous work, Xie and MacKenzie[8] indicated that exchangeable Zn extracted by 0.5 M KNO_3 was reduced in soils treated with P at a initial pH 6.0. This may partly explain the observation that Zn uptake by plants was depressed at high P and high pH levels[9]. However, the mechanisms involved in interactions between P, pH and Zn in soil are still not well understood. There is a lack of information on how pH would affect Zn sorption-desorption and Zn fractions in soils treated with P. The objectives of this study were to evaluate the effects of pH on Zn sorption-desorption and on Zn fractions in soils treated with and without P.

MATERIALS AND METHODS

Soil samples (0-15 cm) from an Uplands sand (Typical Haplorthod[10]), a St. Bernard loam (Typical Eutrochrept), and a Dalhousie clay (Typical Humaquept) identified as UT, ST and DT respectively, ranging in clay content, pH, CEC, organic C and extractable Fe and Al (Table 1), were air-dried and ground to pass a 1-mm sieve.

TABLE 1
Selected Properties of the Experimental Soils

Parameter†	Soil UT	Soil ST	Soil DT	Reference
Clay content, g kg^{-1}	100	200	410	11
pH, soil:water=1:2	6.3	5.3	5.7	12
CEC, mmol(+) kg^{-1}	57.0	119	260	13
Organic C, g kg^{-1}	16.7	26.1	38.8	14
Fe(Al)-DC, g kg^{-1}	3.1(1.1)	9.4(1.5)	9.2(1.9)	15
Fe(Al)-AO, g kg^{-1}	1.5(2.0)	3.7(2.1)	3.1(3.5)	15
Fe(Al)-PP, g kg^{-1}	0.5(0.7)	1.3(1.1)	1.4(2.1)	15

†: DC=dithionite citrate; AO=ammonium oxalate;
PP=sodium pyrophosphate.

Soil samples of 2 g were first equilibrated with 20 ml of P (0 and 9 mM NaH_2PO_4) solutions in 50-ml stoppered polypropylene centrifuge tubes. The initial ionic strength of each solution was controlled using 0.03 M $KClO_4$. The mixture of the soil and the solution was adjusted to initial pH values of 4.5, 6.0 and 7.5 with $HClO_4$ or KOH solutions and such pH values were maintained for 3 h before shaking. Each combination of soilxPxpH was repeated to ensure that every treatment in the third mixing (Fig. 1) was duplicated. Before and after adjusting pH, the tube containing soil and the solution was weighed in order to determine volume changes introduced in the process of adjusting pH. The mixture was mixed for 72 h using an end-over-end shaker in order to achieve a near equilibration (throughout the text, equilibration refers to near equilibration), and centrifuged at

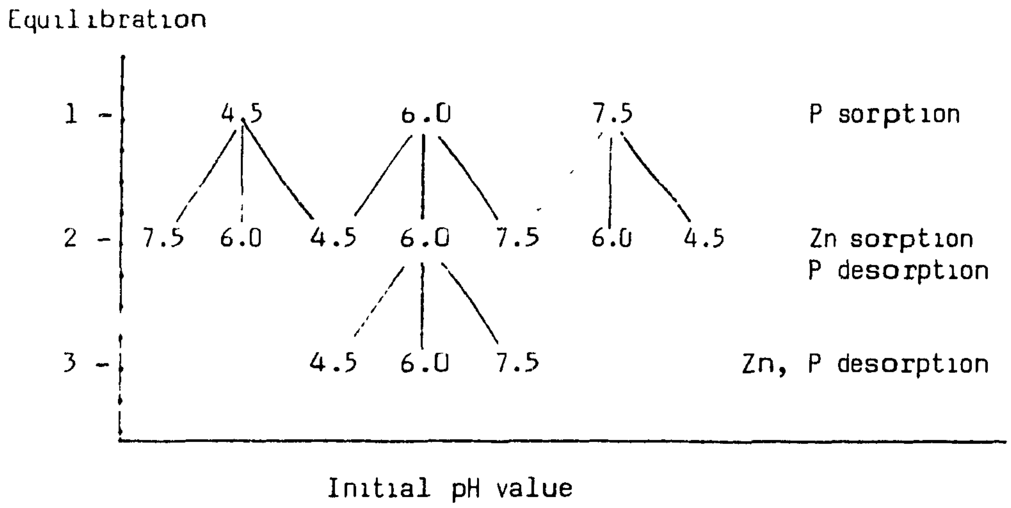

FIGURE 1. Experimental pH Flow Chart for the Sequential Equilibration Procedures.

12,000 rpm for 10 min and filtered through Whatman No. 42 filter paper. Supernatant solutions were kept at 4°C prior to P^{16} and Zn (atomic absorption) analyses and pH (referred as to final pH) reading.

The tube containing soil and residual solution was weighed to determine the amount of P in the interstitial solution. Then 20 ml of Zn solution (0, 0.5 and 1.0 mM $ZnSO_4$ in 0.03 M $KClO_4$) were added for a second 72-h equilibration. The mixture of the soil and the solution was re-adjusted to three pH levels (4.5, 6.0, and 7.5) according to Fig.1 and subsequent steps were as those for the first equilibration.

In a third equilibration, the tube containing soil and residual solution from the second equilibration was weighed and 20 ml 0.03 M $KClO_4$ solution was added. The mixture of soil and solution was adjusted to three pH levels according to Fig. 1 and subsequently mixed for 72 h, and centrifuged as in the first equilibration.

Sorption and desorption values were calculated by substracting the amount of P or Zn remaining in the supernatant from the amount of P or Zn added or remaining from the previous step. Thus P or Zn sorption is defined as P or Zn adsorbed on soil particle surfaces and precipitated from the solution.

Samples at initial pH 6 in the first equilibration, 1.0 mM Zn solution at initial pH 6 in the second equilibration and at initial pH 4.5, 6.0 and 7.5 in the third equilibration were analysed sequentially for the following Zn fractions: 0.5 M KNO_3-extractable Zn (Zn_{KNO3}), 0.5 M NaOH-extractable Zn (Zn_{NaOH}) and concentrated HNO_3 + 30% H_2O_2 (Zn_{HNO3}) at 110°C extractable Zn[17,18]. Before adding each extractant, the tube containing soil sample and residual solution from the previous step was weighed to determine the amount of Zn in the interstitial solution.

The statistical procedures of Steel and Torrie[19], and SAS User's Guide[20] were followed for the LSD test and regression analyses.

RESULTS

Effect of pH and Added P on Zn Sorption

Zinc sorption (Zn_S) was a linear function of the final pH in all of the soils (Table 2). The addition of P slightly enhanced the pH effect on Zn_S in the DT and ST soils and considerably increased the pH effect on Zn_S in the UT soil. Higher Zn addition rates resulted in higher intercept and slope values except for the P-treated UT soil. The intercept values were in decreasing

TABLE 2
Regression between Zn Sorption (Zn_S) and Final pH at the Second Equilibration with and without Added P

Soil	Zn-rate (mM)	P addition			
		Added P, 9 mM		Zero added P	
		Equation†	r^2	Equation	r^2
DT	0.5	$Zn_S=4.38+0.06pH$	0.42^{**}	$Zn_S=4.35+0.05pH$	0.74^{**}
	1.0	$Zn_S=8.16+0.21pH$	0.86^{**}	$Zn_S=7.98+0.24pH$	0.83^{**}
ST	0.5	$Zn_S=4.16+0.10pH$	0.64^{**}	$Zn_S=3.86+0.12pH$	0.76^{**}
	1.0	$Zn_S=6.85+0.43pH$	0.80^{**}	$Zn_S=6.62+0.37pH$	0.86^{**}
UT	0.5	$Zn_S=2.51+0.37pH$	0.55^{**}	$Zn_S=2.93+0.27pH$	$0.38^{††}$
	1.0	$Zn_S=\quad 1.36pH$	0.68^{**}	$Zn_S=4.70+0.61pH$	0.64^{**}

† = Intercept and slope values are significant at 1% level; Zn_S= total Zn sorbed, mmol kg^{-1} soil; each regression was done with 22 pairs of data;
†† = significant at 10% level; ** = significant at 1% level.

order while the slope values were in increasing order for DT, ST and UT soils for both 0 and 9 mM P treatments.

Effect of pH and Added P on Zn Desorption

The addition of P resulted in less Zn desorption (Zn_D) at low pH values in all soils at the third equilibration (Table 3). The amounts of Zn_D with added P were only 41, 49 and 62% of the amounts of Zn_D without added P, for the DT, UT and ST soils, respectively. Differences of Zn_D with or without added P were not pronounced as only small amounts of Zn were desorbed (or resorbed in the UT soil) in either case at initial pH 7.5. High solution pH (initial or final) reduced Zn_D in soils with or

TABLE 3
Effect of Initial and Final pH on Desorption of P and Zn (mmol kg^{-1} soil) at the Third Equilibration

Initial pH	Soil								
	DT			ST			UT		
	pH†	P_D	Zn_D	pH	P_D	Zn_D	pH	P_D	Zn_D
					9 mM P				
4.50	5.64	5.80‡	0.22	5.41	3.78	0.80	5.46	1.97	1.05
6.00	6.04	4.17	0.08	6.19	2.92	0.16	5.92	1.73	0.26
7.50	7.00	3.14	0.02	7.33	2.83	0.02	6.52	1.85	0.03
$LSD_{0.05}$	0.24	0.24	0.03	0.29	0.28	0.13	0.08	0.23	0.23
					Zero P				
4.50	4.20	-	0.54	4.10	-	1.29	5.80	-	2.16
6.00	5.58	-	0.14	5.72	-	0.26	6.37	-	0.35
7.50	8.37	-	0.00	8.28	-	0.09	7.58	-	-0.07
$LSD_{0.05}$	1.61	-	0.08	1.04	-	0.05	1.07	-	0.25

† = final pH values; ‡ = initial Zn level: 1.0 mM.

without added P. The addition of P resulted in a buffering of soil pH compared to zero P addition. In the presence of soils treated with P, the final pH of the three soils tended to move towards pH 7, especially for treatments with initial pH of 4.5 and 7.5. For the DT and ST soils with zero P addition, the final pH of the solution shifted to lower values for treatments with initial pH 4.5 and 6.0 and to higher values for the treatments of initial pH 7.5.

Decreasing initial pH increased P desorption (P_D) in the DT and ST soils (Table 3). In the UT soil, the highest P_D was found with initial pH of 4.5, the lowest with initial pH of 6.0.

Effect of pH and added P on Zn Fractions

Increasing pH decreased Zn_{KNO3} as did added P at pH values of 4.5 and 6.0 (Table 4). For the UT soil, P addition increased Zn_{KNO3} at pH 7.5. Increasing pH with addition of P resulted in more Zn_{NaOH} in all soils tested, and more Zn_{HNO3} in the DT soil. Regression showed that Zn_{KNO3} was a negative linear function of the third final pH (r^2 from 0.66 to 0.94, $p<0.05$). In soils with added P, Zn_{NaOH} was a positive linear function of the third final pH (r^2=0.72, 0.80 and 0.91 respectively, for the DT, ST and UT soils). Increased Zn_{NaOH} and Zn_{HNO3} with added P (differences with and without added P) generally was less (or non-existent) at high compared to low pH values. The Zn_{HNO3} in the UT soil was reduced by P addition at pH 7.5. The sum of the Zn fractions was influenced little by pH but was greater in soils with added P compared to no P addition.

TABLE 4

Effects of P Addition and Initial pH Values on Zn Fractions

Initial pH (Third equilibration)	Fractions†							
	Zn_{KNO3}		Zn_{NaOH}		Zn_{HNO3}		Sum	
	No P	9 mM-P	No P	9 mM-P	No P	9 mM-P	No P	9 mM-P
	mmol kg^{-1}							
				DT				
4.5	1.52	0.46	2.02	2.64	5.23	7.34	8.77	10.44
6.0	0.56	0.24	2.63	2.92	5.62	7.67	8.81	10.83
7.5	0.12	0.11	2.58	3.00	6.35	7.59	9.04	10.71
$LSD_{0.05}$	0.37	0.03	0.08	0.09	0.29	0.19	0.32	0.18
				ST				
4.5	3.28	1.96	0.77	1.76	3.34	6.85	7.39	10.57
6.0	1.81	0.80	1.71	2.53	4.50	6.67	8.03	10.00
7.5	0.24	0.22	2.12	2.73	5.55	6.79	7.91	9.73
$LSD_{0.05}$	0.40	0.37	0.08	0.23	0.23	NS	0.43	NS
				UT				
4.5	2.94	2.29	0.47	2.61	1.84	2.12	5.25	7.03
6.0	2.04	2.09	1.86	3.20	2.70	2.00	6.59	7.30
7.5	0.80	1.34	2.54	3.49	3.14	2.58	6.49	7.41
$LSD_{0.05}$	0.31	0.19	0.16	0.26	0.18	NS	0.34	NS

Over all soils

Zn_{KNO3} = $6.85-0.63 \times pH_3-0.09 \times P_{ad3}$ ($n=18$, $R^2=0.71$, $p<0.01$)
pH_3 = final pH after the third equilibration
P_{ad3} = sorbed P remaining after the third equilibration

† = Initial Zn rate: 1.0 mM; NS = not significant at 5% level.

DISCUSSION

Zn_S and Zn_{HNO3} were in increasing order and Zn_D in decreasing order in UT, ST and DT soils with added P. Soils with high clay, organic matter, Fe and Al contents and CEC have more available reactive sites and are expected to have more specifically sorbed Zn and less Zn_D. In theory, soils with high

Fe, Al and organic matter contents should have more variable charges. Thus pH would be expected to have a strong effect on Zn_S and Zn_D. However, the opposite was observed in the present study, in that with the UT soil (low clay, organic C, Fe and Al contents), pH had strong effect on Zn_S and Zn_D, but not on P desorbed. Added P enhanced this pH effect on Zn_S and Zn_D. Increased Zn_{KNO3} with added P at high pH in the UT soil suggested that in soil with low variable charge components, added P influenced Zn reactions perhaps in association with permanent charge sites. Increased Zn_S with increases in pH values was consistent with the results of Barrow[21], who noted that increased $ZnOH^+$ strongly correlated with Zn_S. In addition, the fact that Zn_{KNO3} was significantly reduced by high pH values, compared with low pH values, while Zn_{NaOH} increased confirmed, transformation among Zn fractions with pH changes.

Added P increased Zn_S slightly at the second equilibration (mainly the UT soil) but the P effect was most obvious in Zn fractions, where the sum of the Zn fractions was always greater with added P. The role played by sorbed P in increasing Zn_S in the DT and ST soils was probably not associated with P induced negative charges[7], particularly as the Zn_{KNO3}, or exchangeable Zn, was reduced with added P at low pH values. Added P increased Zn_{NaOH}, which would be related to Zn specifically adsorbed on Fe and Al hydroxides and on organic matter, and increased Zn_{HNO3}, or residual Zn.

The relatively large increase in Zn_{NaOH} with added P in the

UT soil was consistent with the notion of added P acting as a "bridge" between soil surfaces and sorbed Zn[5], or with the mechanism proposed by Kuo and McNeal[4] where sorbed P altered soil surface properties sufficiently to increase Zn_S or decrease Zn_D. The latter seems more likely, as Zn_D was not directly related to P_D, as would be expected from the bridge theory. Similar P effects on Zn_S found in the Zn_{HNO3} fraction (residual Zn) were indications that specifically sorbed Zn has a variety of sorption mechanisms associated with differing soil materials.

The fact that the effect of added P on increasing Zn_{NaOH} and Zn_{HNO3} was most pronounced at low initial pH values could be related to more positive charges on Fe and Al oxides at low pH values, resulting in enhanced P sorption, and consequently, enhanced P-Zn interactions. However, a buffer effect of added P was evident since final pH ranges were reduced with added P, and further, Zn_{KNO3} was associated more with pH at the third equilibration than with P_{ad3} (slope values in Table 4), indicating that the P effect is expected only at low pH values. At high pH values, such effects became less important. On one soil (UT) where such comparisons are possible, P effects on Zn_{NaOH} were more pronounced at low pH values. Thus the mechanism of P induced Zn sorption in terms of Zn_{NaOH} may well be a function of pH.

ACKNOWLEDGEMENTS

The financial support from the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

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Appendix III

THE EFFECT OF pH ON ZINC TRANSFORMATION IN AUTOCLAVED SOILS TREATED WITH PYROPHOSPHATE

Key words: pH buffer, pyrophosphate sorption-desorption, Zn sorption-desorption, KNO_3-extractable Zn, NaOH-extractable Zn.

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ABSTRACT

Zinc solubility in soils can be affected by both pH and pyrophosphate (PP), yet the reaction of PP is influenced by pH, thus there is a need to evaluate pH effect on Zn transformation in soils treated with PP. Samples of three autoclaved soils, a Dalhousie (DT) clay, a St. Bernard (ST) loam, and an Uplands (UT) sand were equilibrated first with PP (0.0 and 9.0 P mM), then with Zn (0.0, 0.5, 1.0 Zn mM) and followed by 0.03 M $KClO_4$ solutions at the initial pH of 4.5, 6.0, and 7.5 with constant ionic strength. The first equilibration was for PP sorption, the

second for Zn sorption and PP desorption, and the third for Zn desorption and further PP desorption. And finally, Zn of selected samples were extracted with 0.5 M KNO_3 (exchangeable Zn, Zn_{KNO3}), 0.5 M NaOH (organic and Fe oxides associated Zn, Zn_{NaOH}) solutions, and concentrated $HNO_3+H_2O_2$ (residual Zn, Zn_{HNO3}).

Increases in pH reduced PP sorption in the UT and the ST soils while high or low pH values tended to reduced it in the DT soil, indicating a competition between PP and OH ions for sorption sites. Zinc sorption was linearly related to solution pH, the slopes varied from 0.10 to 1.06, lower values were associated with PP addition, with low Zn rate, with finer textured soils, with high contents of Fe and Al materials, and with high pH buffer capacity. The values of Zn desorption and Zn_{KNO3} were greater at low than high pH while the reverse was true for Zn_{NaOH}. The pH effects on Zn sorption-desorption and fraction distributions were less significant in soil with than without PP. The overall effect of high pH and the presence of the sorbed PP was the increased Zn specific sorption, compared to the pH or PP effect alone.

INTRODUCTION

The effect of pH on Zn reactions in soils has been studied extensively (9, 16, 23). It was generally accepted that high pH values decrease Zn solubility as a result of increasing Zn sorption both through increasing Zn adsorption and through increasing Zn precipitate (11, 15, 23). The mechanism of increasing Zn sorption with raising pH increasing Zn sorption was not well understood. Barrow (3) believed that high pH increases the proportion of $ZnOH^+$ species, and it is the $ZnOH^+$ reacting with the sites of negatively charged surface. Tiller et al. (23) showed evidence that increases in pH resulted in increases in Zn specific sorption.

Orthophosphate (OP) was shown to enhance Zn sorption both directly or indirectly (4, 18, 24). The direct effect includes the sorbed OP increases Zn sorption sites (24) or precipitates Zn from the solution (11), the indirect effect includes OP addition alternating soil pH (4, 18) thus affecting Zn sorption. In a study of OP-pH-Zn interaction in soils (25), the OP effect was found to be more significant at low than at high pH conditions, and OP was shown to increase Zn specific sorption as did high pH condition, as indicated by the decreased KNO_3-extractable and the increased NaOH-extractable Zn.

Studies on pyrophosphate (PP) and Zn interaction are numerous in the last two decades. The PP effect on Zn solubility could be summarized as (i) PP increases Zn solubility through the chelating effect (5, 8, 14), and the effect is more significant at high pH conditions while in most agricultural soils the pH value is within a range of 5-8, but the effect is limited due to the rapid hydrolysis of PP (7), (ii) has no effect on Zn solubility, and (iii) decreases Zn solubility through increasing Zn specific sorption at a constant initial pH (8, 10, 17, 26) or increasing Fe solubility and forming Fe-Zn precipitates (12, 15). In soils, there exist shifts of $H_4P_2O_7$ --> $H_3P_2O_7^-$ --> $H_2P_2O_7^{2-}$ --> $HP_2O_7^{3-}$ --> $P_2O_7^{4-}$ and Zn^{2+} --> $ZnOH^+$ --> $Zn(OH)_2$ as solution pH increases (11), the shifts are in the reverse direction as pH decreases. Little information is available on PP-pH-Zn interaction in soils. A bridge effect of the sorbed OP was proposed for OP (6, 21), in which, Zn ion is attached to sorbed OP. However, desorption study at various pH values did not show evidence of the existence of such bridge effect (25). Whether the bridge effect is in association with PP remains to be investigated. Since PP (1) or Zn (3, 16) sorption has been shown to be a function of pH, and the proportion of $P_2O_7^{4-}$ species, which complexes cations, is greater at high than at low pH values, understanding the overall effect of PP-pH-Zn interaction in soil would be helpful in improving Zn nutrition status of crops grown in soils with PP fertilization.

The objectives of this study were to evaluate the pH effect on Zn sorption, desorption, and fraction distribution in autoclaved soils treated with or without PP.

MATERIALS AND METHODS

Topsoil samples from an Uplands sand (Typical Haplorthod) a St. Bernard loam (Typical Eutrochrept), and a Dalhousie clay (Typical Humaquept), identified as UT, ST and DT respectively, ranging in CEC, clay, and organic C and extractable Fe and Al contents, were autoclaved (26) and accessed in this study.

To weighed 50 ml polyethylene centrifuge tube, 2 g soil sample was added, the soil was moist to 0.33 kPa suction and autoclaved at 121°C and 15 kPa for 1 h day^{-1} for 3 days to eliminate microbial and enzymatic activities. After autoclaving, the weight was recorded. Three equilibria between the autoclaved soil and 20 ml PP (0.0 and 9.0 P mM as $Na_4P_2O_7.10H_2O$), then 20 ml Zn (0.0, 0.5, 1.0 mmole Zn kg^{-1} as $ZnSO_4.7H_2O$), and finally 20 ml of 0.03 M $KClO_4$ solution were carried out sequentially. The PP and Zn solutions were prepared in 0.03 M $KClO_4$. Two drops of toluene were added to the solution-soil suspension. Initial pH value of the suspension for each equilibration was adjusted to

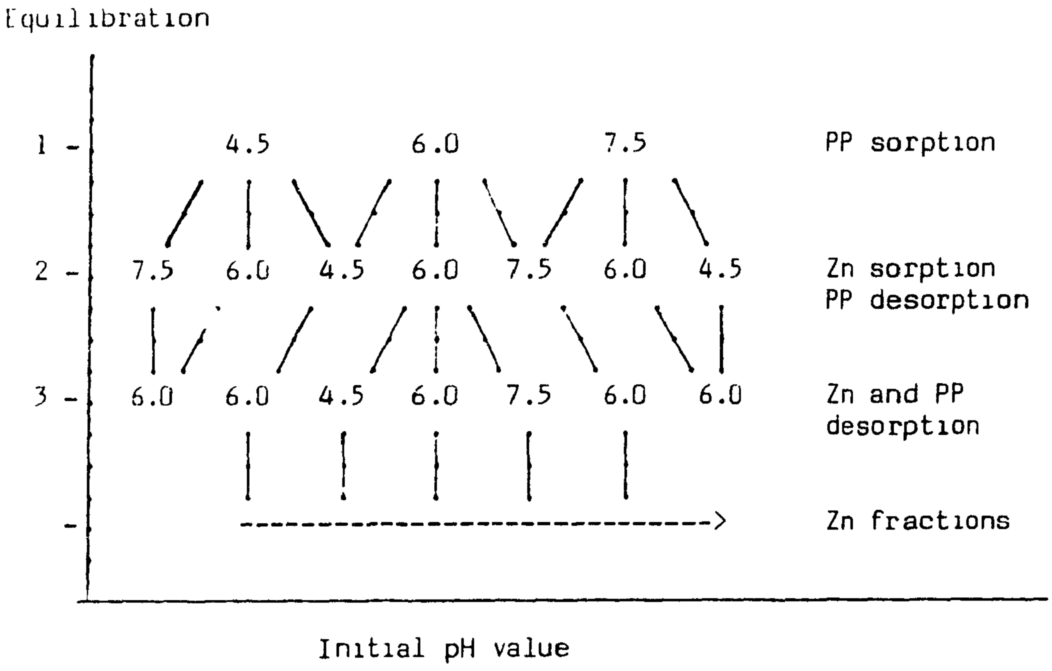

FIGURE 1. Experimental pH flow chart for the sequential equilibration procedures.

4.5, 6.0, and 7.5 (Fig. 1), using $HClO_4$ or KOH solutions, and such pH values were maintained for 3 h before shaking. Before and after adjusting pH, the tube containing soil and the solution was weighed in order to determined volume changes introduced in the process of adjusting pH. The suspension in the stoppered tube was mixed for 72 h using an end-over-end shaker in order to achieve a near equilibration, and centrifuged at 12,000 rpm for 10 min and filtered through Whatman No. 42 filter paper. Supernatant solutions from each equilibration were received in polyethylene bottles and kept at 4°C prior to PP, OP (2), Zn (atomic absorption) analyses and pH (referred to as pH_1, pH_2, and pH_3 for the first, the second, and the third equilibration, respectively) readings. The first equilibration determined PP sorption (PP_{S1}), the second Zn sorption (Zn_{S2}) and PP desorption (PP_{D2}), and the third Zn desorption (Zn_{D3}) and further PP desorption (PP_{D3}). Sorption and desorption values were calculated by subtracting the amount of PP or Zn remaining in the solution from the total amount of the previous step. Thus PP or Zn sorption was defined as PP or Zn adsorbed on soil particle surface and precipitated from the solution. The dissociation constants of $\log k_1=-0.80$, $\log k_2=-2.28$, $\log k_3=-6.70$, and $\log k_4=-9.41$ (11) were used to calculate PP species distribution as functions of pH in solutions.

Samples at initial pH 6 in the first equilibration, 1.0 mM Zn solution with initial pH 4.5, 6.0, and 7.5 in the second and the third equilibrations were analysed sequentially for the following Zn fractions: 0.5 M KNO_3- (ZN_{KNO_3}), 0.5 M NaOH-

(Zn_{NaOH}) and concentrated HNO_3 + 30% H_2O_2 (Zn_{HNO3}) at 110°C extractable Zn (13, 20). Before adding each extractant, the tube containing soil sample and residual solution from the previous step was weighed to determine the amount of Zn in the interstitial solution.

The sorption, desorption and fraction data were expressed on oven (105°C) dry basis. The statistical procedures of Steep and Torrie (22) were followed for the LSD test and regression analyses.

RESULTS AND DISCUSSION

Soil pH did not remain at the initial pH values after equilibration with PP solutions but tended to increase and the values of increased pH were greater at low than at high initial pH (Table 1). Two mechanisms may have associated with the increased pH. (i) After the addition of $Na_4P_2O_7$ to the autoclaved soils, there would be a reaction of $P_2O_7^{4-} + 2H_2O <==> HP_2O_7^{3-} + H_3O_2^-$ (logk=-4.59), such produced OH^- may have caused the increases in solution pH. (ii) PP specific sorption occurred, i.e., PP ions replaced OH^- groups from the sorbent surface, increasing the solution pH. The specific sorption was less significant (less increased pH) at high initial pH value probably due to the competition between OH^- and PP ions for sorption sites.

Pyrophosphate sorption increased as decreases in solution pH in the UT and the ST soils, while in DT soil, PP_{S1} tends to be a quadratic function of the solution pH (Table 1), within the pH range of 5 to 8 observed in normal agricultural soils, the effect was more significant at lower than at higher pH values, indicating that more sites for PP sorption were available on the surface of soil particles at low than at high pH, or that PP was mainly sorbed through electrostatic attraction between the surface and PP ions.

The changes in proportion of PP species with pH are indicated in Fig. 2, within the pH range of 5-8, the species of $H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$ are in the ranges of 0.08-0.00, 5.21-0.06, 79.93-17.96, 14.60-65.90, and 0.18-16.09% of the total PP, respectively, suggesting that the species associated with PP sorption be $H_2P_2O_7^{2-}$ - $HP_2O_7^{3-}$ over the pH range. These PP species may reach the sorbent surface under the

TABLE 1
Pyrophosphate Sorption (PP_{S1}, mmole P kg^{-1} soil) and pH (pH_1) after 72 hr Equilibration.

Initial pH	Soil					
	Uplands		St. Bernard		Dalhousie	
	pH_1	PP_{S1}	pH_1	PP_{S1}	pH_1	PP_{S1}
4.5	5.43	59.0	5.11	70.7	5.42	79.6
6.0	6.35	44.1	6.48	58.2	7.16	80.7
7.5	7.34	37.3	7.64	50.3	7.95	78.7
$LSD_{0.05}$	0.04	1.3	0.07	2.1	0.08	1.5

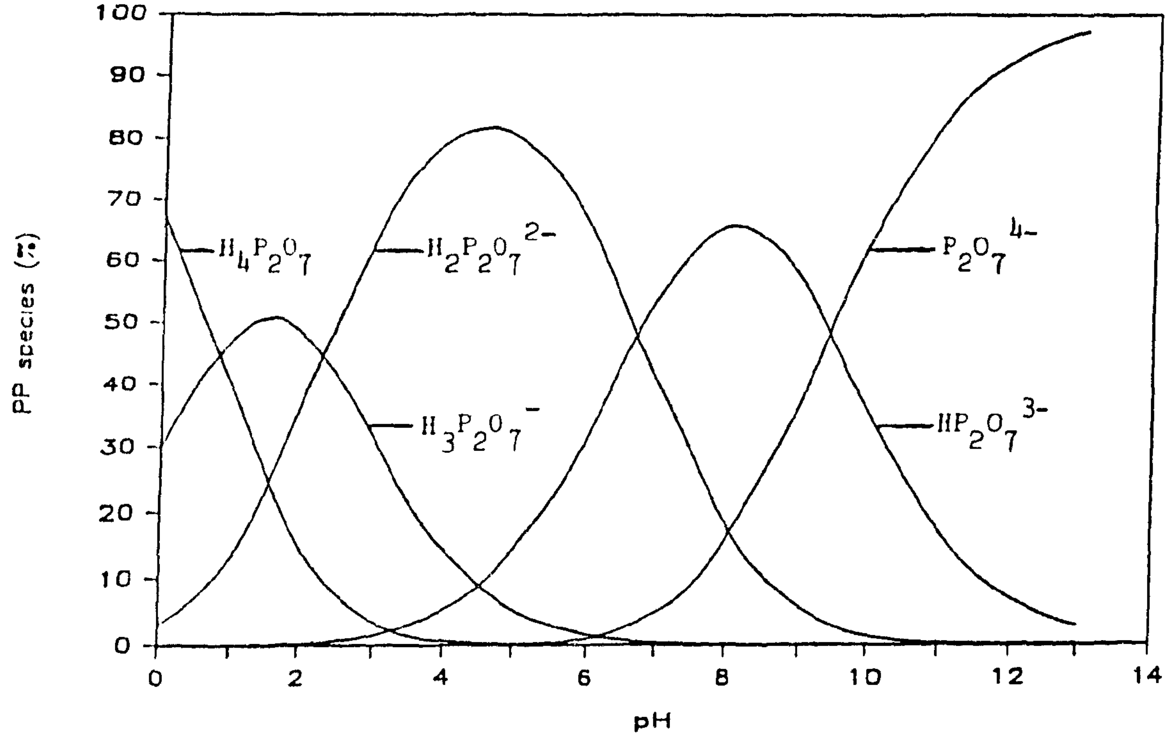

FIGURE 2. Proportion of pyrophosphate (PP) species as related to pH.

driving force of H-binding or van de Waal force (19).

Pyrophosphate sorption was not only controlled by pH. More PP was sorbed in the finer than in the coarser textured soils (Table 1), which is in consistent with the concept that the finer the soil textures, the greater are the surface areas or the more are the sorption sites, is also consistent with more contents of Fe and Al materials in the finer than in coarser textured soils (26), suggesting that Fe and Al components be involved in accommodating PP. Furthermore, the pH effect was more significant in the coarser than in the finer textured soils, e.g., in the pH range of 5.0-6.5, a unit decrease in pH in the UT soil resulted in an increase in PP sorption of 16 mmole P kg^{-1} soil, the value in the ST soil was 9 mmole P kg^{-1} soil, while the value in the DT soil was not significant, suggesting that the pH effect on alternating the number of sorption sites was more significant in the coarser than in the finer textured soils, or the coarser textured had less pH buffer capacity.

Zinc sorption increased as the the increases in solution pH in soils with and without PP except in the DT soil with sorbed PP (Table 2). The regression between Zn_{S2} and pH_2 indicated that pH effect on Zn sorption was greater with high than with low Zn addition rate, in the coarser than in the finer textured soils, which were consistent with the work on OP (25), and in soils with less than with more Fe and Al contents, suggesting that free Fe or Al may have precipitated Zn from the solution (15), and was less significant in soils with than without sorbed PP, indicating that PP sorption reduced pH effect on Zn sorption, while OP was shown to increase pH effect on Zn sorption (25). One of mechanisms associated with Zn sorption is that Zn ions replace protons on the sorption sites, the displaced protons in the solution has potential of decreasing pH. More Zn is sorbed in soils with than without sorbed PP, thus there should be more displaced proton in the solution if both the sorbed PP and the PP remaining in the solution had no effect on buffering soil pH. In

TABLE 2

Zinc Sorption (Zn_{S2}) as a Function of pH (pH_2) at the Second Equilibration in Soils Treated with and without Pyrophosphate.

Soil	Zn-rate	Equation	r^2
		90 mmole P kg^{-1}	
Uplands	0.5	$Zn_{S2}=3.90(\pm0.31)+0.14(\pm0.05)pH_2$	0.48^{*}
	1.0	$Zn_{S2}=6.27(\pm0.31)+0.47(\pm0.05)pH_2$	0.91^{**}
St. Bernard	1.5	$Zn_{S2}=4.14(\pm0.18)+0.10(\pm0.03)pH_2$	0.59^{**}
	1.0	$Zn_{S2}=7.62(\pm0.32)+0.31(\pm0.05)pH_2$	0.81^{**}
Dalhousie	0.5		NS
	1.0		NS
		Zero added P	
Uplands	0.5	$Zn_{S2}=1.78(\pm0.41)+0.40(\pm0.07)pH_2$	0.80^{**}
	1.0	$Zn_{S2}=1.77(\pm0.62)+1.06(\pm0.12)pH_2$	0.91^{**}
St. Bernard	0.5	$Zn_{S2}=3.36(\pm0.07)+0.21(\pm0.01)pH_2$	0.98^{**}
	1.0	$Zn_{S2}=5.65(\pm0.16)+0.54(\pm0.03)pH_2$	0.98^{**}
Dalhousie	0.5	$Zn_{S2}=4.64(\pm0.12)+0.05(\pm0.02)pH_2$	0.50^{*}
	1.0	$Zn_{S2}=8.41(\pm0.17)+0.21(\pm0.03)pH_2$	0.88^{**}

Zn_{S2} = Zn sorbed at the second equilibration, mmole kg^{-1} soil;

ns not significant at 0.05 level;

* significant at 0.05 level;

** significant at 0.01 level.

fact, the pH tended to shift towards 6 or near neutral values in most cases in the presence of PP, especially at low pH with low Zn addition rate (Tables 3, 4). Thus for each unit charge in solution pH (when the pH_2 is expressed as a function of Zn_{S2}),

TABLE 3

Effect of Initial pH at the Third Equilibration on Final pH (pH_3) and Desorption of PP (PP_{D3}) and Zn (Zn_{D3}, mmole P or Zn kg^{-1} soil).

Initial pH†	Soil								
	Dalhousie			St. Bernard			Uplands		
	pH_3	PP_{D3}	Zn_{D3}	pH_3	PP_{D3}	Zn_{D3}	pH_3	PP_{D3}	Zn_{D3}
	90 mmole P, 5 mmole Zn kg^{-1}								
4.50	6.30	8.13	0.04	6.33	8.89	0.10	5.94	1.96	0.12
6.00	6.47	8.41	0.04	6.29	9.95	0.10	6.21	2.27	0.12
7.50	6.35	8.71	0.04	6.44	9.12	0.10	5.89	2.16	0.12
$LSD_{0.05}$	NS	NS	NS	0.04	NS	NS	NS	NS	NS
	Zero P, 5 mmole Zn kg^{-1}								
4.50	4.10	-	0.20	4.18	-	0.45	4.24	-	0.71
6.00	6.00	-	0.02	5.89	-	0.11	5.05	-	0.33
7.50	7.83	-	-0.00	7.31	-	0.02	7.19	-	-0.00
$LSD_{0.05}$	1.00	-	0.03	0.44	-	0.03	0.67	-	0.07
	90 mmole P, 10 mmole Zn kg^{-1}								
4.50	4.37	10.7	0.32	4.47	8.4	0.61	4.44	2.35	1.36
6.00	6.12	7.5	0.12	6.19	10.8	0.26	5.09	3.06	0.42
7.50	7.67	5.5	0.08	7.65	8.0	0.18	7.21	3.89	0.06
$LSD_{0.05}$	0.39	0.6	0.07	0.74	NS	0.06	0.54	1.10	0.05
	Zero P, 10 mmole Zn kg^{-1}								
4.50	4.36	-	0.47	4.13	-	1.10	4.12	-	1.79
6.00	6.01	-	0.15	5.77	-	0.35	4.85	-	0.83
7.50	7.46	-	0.02	7.26	-	0.04	6.92	-	0.04
$LSD_{0.05}$	0.43	-	0.02	0.38	-	0.14	0.24	-	0.60

† Initial pH values for the first and the second equilibration were 6.0.

TABLE 4

Effect of pH on Zn Fractions in Soils Treated with or without Pyrophosphate (PP) (Zn rate=10 mmole Zn kg^{-1}).

Initial pH		pH_2		pH_3		Zn_{KNO3}		Zn_{NaOH}		Zn_{HNO3}	
2nd	3rd	-PP[1)]	+PP	-PP	+PP	-PP	+PP	-PP	+PP	-PP	+PP
						mmole kg^{-1}					
						Dalhousie					
4.5	6.0	4.4c	6.6b	5.7d	6.3bcd	0.65b	0.18e	2.11f	3.04ab	4.90bc	4.55c†
6.0	4.5	6.4b	6.5b	4.4e	4.4e	0.99a	0.45c	2.04f	2.80c	4.88bc	5.31ab
6.0	6.0	6.5b	6.5b	6.0cd	6.1bcd	0.47c	0.14e	2.48de	3.01b	5.21abc	5.46ab
6.0	7.5	6.4b	6.5b	7.5a	7.7a	0.17e	0.06f	2.60d	3.05ab	5.65a	5.36ab
7.5	6.0	7.8a	8.1a	6.7b	6.5bc	0.29d	0.10ef	2.43e	3.16a	5.66a	5.42ab
						St. Bernard					
4.5	6.0	4.3d	4.8c	6.0de	5.5f	1.85b	0.75de	1.31f	2.57b	3.64e	4.07d
6.0	4.5	6.1b	6.2b	4.1g	4.5g	2.82a	1.29c	0.96g	2.33c	3.45e	4.06d
6.0	6.0	6.3b	6.1b	5.8ef	6.2d	1.83b	0.41f	1.55e	3.11a	4.07d	4.35c
6.0	7.5	6.3b	6.3a	7.3b	7.7a	0.61ef	0.12g	2.01d	3.19a	4.58bc	4.48bc
7.5	6.0	7.6a	6.1b	6.6c	6.2cd	0.97d	0.41f	1.91d	3.08a	4.97a	4.71ab
						Uplands					
4.5	6.0	4.3e	4.7d	4.4ef	4.7de	2.45a	1.89b	0.49g	2.54c	1.50c	2.03bc
6.0	4.5	4.5de	5.7b	4.1f	4.4e	2.67a	2.38a	0.43g	2.19d	1.63c	1.75bc
6.0	6.0	5.1c	6.0b	4.9cd	5.1c	2.45a	1.70bc	1.01f	3.42b	3.58a	2.19abc
6.0	7.5	4.7d	5.9b	6.9a	7.2a	1.37de	0.63f	1.83e	3.94a	2.57abc	2.45abc
7.5	6.0	7.5a	7.6a	6.4b	6.3b	1.48cd	1.11e	3.22b	3.93a	3.16ab	2.42abc

† means with same letter(s) in each column under a soil are not significantly different at the level 0.05 by LSD test.

1) +PP =added PP at 90 mmole P kg^{-1}, -PP =zero added PP.

more Zn would be sorbed with PP than without PP as a result of the pH buffer ability of PP. The initial pH at the third equilibration did not show any effect on PP_{D3} or Zn_{D3} in soils with 5 mmole added Zn kg^{-1}, apparently due to the fact that in the presence of PP, soil pH was buffered, but at the rate of 10 mmole kg^{-1}, the pH effect on PP desorption was basically significant.

The pH effect on PP_{D3} was not consistent in different soils. In the DT Soil, more PP_{D3} was associated with low pH, while in the UT soil, more PP_{D3} was associated with high pH, and in the ST soil, more PP_{D3} was with the medium pH value (Table 3). The pH effect on Zn_{D3} was consistent in all soils with and without PP, but was less apparent in soils with than without PP. Low pH resulted in more Zn_{D3}, the effect was less significant at high pH (> 7). The relationships among pH_3, Zn_{D3} and PP_{D3} did not support the speculation that the increased Zn sorption was attached to the sorbed PP, i.e., the bridge effect. If such mechanism was in operation, then the increased Zn_{D3} should be in a positive proportion to the increases in PP_{D3} and to the increases in pH. As observed in soils with added OP (25), in the autoclaved soils, more Zn_{D3} occurred in the coarser than in the finer textured soils (Table 3) although the Zn_{S2} values were smaller with the former than with the later soils (Table 2), indicating that Zn was less strongly sorbed in the coarser than in the finer soils.

Zinc fractions were affected by both the second and the third initial pH values (Table 4), indicating that pH change at anytime in farming practice would introduce Zn fraction redistribution, with the addition of PP, the redistribution was less obvious. Higher pH values resulted in less Zn_{KNO3} and more Zn_{NaOH} in the autoclaved soils treated with and without PP, with PP addition decreasing Zn_{KNO3} and increasing Zn_{NaOH}. Comparison among the treatments of second initial pH 6.0 and the third initial pH 4.5, 6.0, and 7.5 showed that for the Zn_{KNO3}, the differences between without and with PP were greater at low than at high pH values for the DT and ST, but the reverse was true for the UT soil, indicating that the effect of PP on increasing Zn specific sorption was most important in soils of low pH or high pH depending on individual soil, while the comparisons among the treatments of the second initial pH 4.5, 6.0, and 7.5 and the third initial pH 6.0 showed that for the Zn_{KNO3}, the greatest difference between without and with PP was associated with the second initial pH 6.0 in the ST and UT soils. The significant lower Zn_{KNO3} values in soils of high pH with PP compared to zero PP suggested that Zn deficiency may become more severe in soil of the high pH when PP fertilizer is applied if the Zn_{KNO3} is considered as available form for crop uptake. The fact that both the high pH condition and the presence of PP resulted in more less Zn_{KNO3} and more Zn_{NaOH} is consistent with the speculation that both the OH groups on the surface of sorbent and the sorbed PP were the sites for Zn specific sorption to occur. Since NaOH also extracts Zn associated with Fe or Al components, these results suggested that the PP-pH-Zn interaction occur on surface of Fe and Fe minerals. Low pH showed a general trend of reducing Zn_{HNO3} (Table 4). The differences between with and without PP were not significant except in the ST soil of low pH where the presence of PP increased Zn_{HNO3}.

CONCLUSIONS

The decreased Zn solubility with the increases in pH in the presence of sorbed PP was attributed to the increased Zn specific sorption as indicated by increased Zn sorption, reduced Zn desorption and KNO_3-extractable Zn, and the increased NaOH-extractable Zn in soils. These effects were more significant at low than at high pH values. Sorbed PP depressed pH effect on Zn transformation, which may have been associated with high (or relatively high) pH buffer capacity of soils with sorbed PP.

ACKNOWLEDGMENTS

The financial support from the Natural Science and Engineering Research Council of Canada for this study (grant No. OGPIN 003) is greatly appreciated.

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