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PHOSPHATE ADSORPTION AND DESORPTION ON TWO CONTRASTING SOILS USED FOR LAND TREATMENT OF WASTEWATER

STEPHEN ARTHUR GASIOROWSKI

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University of New Hampshire

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PHOSPHATE ADSORPTION AND DESORPTION
ON TWO CONTRASTING SOILS
USED FOR LAND TREATMENT OF WASTEWATER

by

STEPHEN A. GASIOROWSKI
B.A. (Chemistry), Colby College, 1976

A DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
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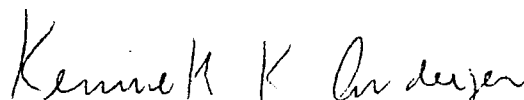
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September 1980

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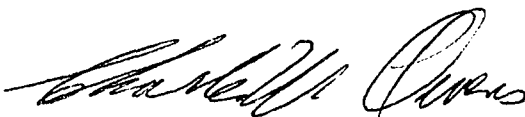
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Date July 30, 1980

This dissertation is dedicated
to my parents and to Mary
who were always confident that I would write it.

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Steph A. Szwedowski

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ABSTRACT

PHOSPHATE ADSORPTION AND DESORPTION
ON TWO CONTRASTING SOILS
USED FOR LAND TREATMENT OF WASTEWATER

by

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University of New Hampshire

September, 1980

Land treatment of wastewater involves the use of plants and the soil to remove unwanted constituents. Removal of phosphorus is particularly important to avoid excessive biological activity in water systems receiving the treated wastewater. This research examines the phosphate adsorption - desorption behavior of two soils: Charlton silt loam, a typical acid soil from New England which is being used in experimental wastewater treatment, and Tujunga coarse sandy loam from a wastewater land treatment facility located at Manteca, California, which has failed to remove phosphate from wastewater efficiently.

The effects of changing the pH and phosphate content of municipal wastewater on adsorption and desorption were determined. Sorption isotherms were determined for each soil using wastewater as the equilibration solution. Phosphate was added to the wastewater to obtain the concentration range necessary for the isotherms. After 96 hour equilibration periods, radioactive phosphorus was added to the suspensions. Measurements of the redistribution of the P-32 were used to determine the exchangeability of the sorbed phosphate.

Radioactive phosphorus-32 was used to follow the adsorption and desorption rates in suspensions of soil and wastewater. Parallel experiments were conducted in which phosphate concentrations were determined by conventional spectrophotometric analysis. Effluent from a conventional secondary treatment facility and the whole soil (all particles < 2 mm) were used in these studies to model the normal situation in land treatment facilities. Concentration changes of solution phosphate or P-32 were measured over 46 hour equilibration periods. After this period, soil samples were separated from the suspension, treated to remove interstitial solution, and dried at room temperature.

The dried soil samples were resuspended with either a fresh portion of effluent or 0.005 M NaCl solution.

Resuspension with effluent mimics a repeat application of wastewater to a treatment field. Suspension in sodium chloride solution allows determination of phosphate desorption in the absence of exchange reactions.

The complementary use of P-32 and non-radioactive phosphate permitted the evaluation of adsorption and desorption of freshly sorbed and native phosphate independently as well as the amount of exchange occurring.

Charlton soil sorbed large amounts of phosphate with a capacity of over 1000 mg P/g soil. At concentrations typical of wastewater, complete removal of phosphate from solution was rapid. When small amounts (<100 mg/g) were sorbed, phosphate was bound in very stable forms which were largely unavailable to exchange. Sorption was slightly less complete in suspensions at pH 8.0 as compared to pH 5.0 and 6.5. At higher loadings of phosphate, an increasing amount of exchangeable phosphate was sorbed on the Charlton soil. However, at a single pH, the proportion of exchangeable phosphate to sorbed phosphate was constant at all amounts of sorbed P studied.

Tujungua soil capacity for phosphate was much lower than Charlton soil. Sorbed phosphate was susceptible to a large amount of exchange as well as net desorption. Efficiency of sorption decreased with a decrease in pH - opposite to the

trend observed with the Charlton soil. A three step mechanism of P sorption was used to explain the results of these studies.

Determination of relative concentrations of Fe (II) and Fe (III) by Mossbauer spectroscopy was examined. Mossbauer spectra were obtained which demonstrate the successful application of the technique to the study of reduced iron in soils.

CHAPTER I

AN OVERVIEW OF LAND TREATMENT OF WASTEWATER

Land Treatment of Wastewater

Land treatment of wastewater involves the use of plants and soil to remove dissolved substances from wastewater. The concept of wastewater renovation by land application has been employed throughout history (Iskandar, 1978). The handling of large amounts of municipal waste by land application became fairly common in Europe during the last century. "Sewage farms" were widely used in Great Britain in the late 19th and early 20th centuries. These facilities were gradually abandoned due to the large land requirements and the production of offensive odors. Both of these problems were minimized by artificial means of sewage treatment which eventually replaced the farms (Cooke, 1978). While land disposal of livestock waste continues in Britain, (more for the reuse of nutrients on farmland than actual "disposal"), use of land in sewage treatment in Britain is limited to the disposal of sewage sludge generated by artificial sewage treatment.

One of the earliest established municipal sewage treatment sites in the United States is located in Calumet, Michigan. Started in 1887, the system continues to operate today with expansion and modification necessary to accommodate increased demands from the areas served (Baillod, et al., 1976). A number of other major facilities for land treatment of wastewater have been established since the last century in the United States and elsewhere (Reed, et al., 1972).

The growth in concern with water system quality is reflected in the Federal Water Pollution Control act and Amendments. Due to this increased concern, the viability of land treatment of wastewater has been examined in much greater detail than previously. A variety of state and federal agencies have been involved in these studies including the U.S. Army Corps of Engineers (Baillod, et al., 1976, Reed, et al., 1973). Several international symposia have been held in recent years on the subject of land treatment of wastewater. A diversity of topics are presently of concern in land treatment systems: legislative requirements, public acceptance, site selection, necessary pretreatment of wastewater, mathematical modeling of transport of materials in the soil, health considerations, and cost requirements.

Before application to land, wastewater is usually treated to the secondary level (i.e. flocculation of particulates and biological removal of other constituents). The method of application may involve spray irrigation, overland flow, or other methods. The rate of application varies among the particular systems. Wastewater may be applied at a rate low enough to allow rapid and complete infiltration, avoiding the accumulation of standing water. An alternative method applies wastewater at a rate which causes flooding of the land area, often to a depth of a few inches. The important factors influenced by the rate of application are; availability of atmospheric oxygen to the soil and bacterial colonies therein, possible changes in soil chemistry associated with saturated conditions, effects on plant growth in the treatment area, and the wastewater/soil contact time. The choice of application method and rate depend on the permeability of the soil, characteristics of the wastewater, and properties of the soil and plants at the particular treatment site.

Reuse of wastewater on forest soils, aiding in the production of timber, is an alternative that minimizes the introduction of toxic materials into the foodchain, although other impacts on the environment are still of concern (Ballard and Fiskell, 1974; Urie, et al., 1978). The possible detrimental effects on tree growth must still be considered but since foodstuffs are not involved, some problems of toxicity at higher levels of the foodchain are

minimized. Sopper and coworkers at the Pennsylvania State University have conducted extensive studies on the effects of land disposal of wastewater on forest areas (Sopper and Kardos, 1973; Sopper and Richenderfer, 1979).

The effects of introducing wastewater into groundwater have received very little attention. The problem of contamination appears much lower than with surface water since percolation through the overlying soil and rock results in physical and chemical removal of some contaminants prior to reaching groundwater level (Dryden and Chen, 1978; Jones and Lee, 1979). Since the disposal of wastewater on land ultimately results in the treated water reaching groundwater, larger scale studies must eventually be made to determine the long term effects of such disposal.

This brief overview of wastewater land treatment presents only the basic considerations of this method of sewage disposal. The great amount of ongoing work indicates high interest and incomplete knowledge of the exact soil - wastewater interactions. This is hardly surprising when one considers the extremely complex and highly variable nature of both soils and wastewater as well as the variability of conditions under which the treatment is carried out.

Phosphorus in Wastewater

Phosphorus contamination of aquatic systems by the introduction of phosphate-containing wastewater has been clearly established as a factor leading to eutrophication (Sawyer, 1966). Phosphate is a key nutrient controlling the growth of algae, which in turn affects water oxygen content, turbidity, and other water quality parameters. A phosphate-phosphorus concentration of 0.03 mg/L or more has been shown to promote eutrophication of lakes (Sawyer, 1966).

Industrial and domestic wastewater is the greatest source of phosphorus in aquatic systems. The phosphate content of wastewater effluent varies considerably but generally falls into the range of 0.5 to 40 mg/L, averaging approximately 10 mg/L (Bouwer and Chaney, 1974).

Phosphate containing detergents represent the largest single source of phosphate in domestic wastewater. The steady decrease of phosphate levels observed at many locations over the past decade has been related to the increased use of non- or low-phosphate detergents (Gakstatter, et al., 1978).

Since most wastewater ultimately enters surface fresh water or groundwater systems, minimization of the phosphate content of effluent from treatment facilities is of major concern. Typically, phosphate is partially removed from the

raw wastewater during the treatment process by precipitation with various chemicals including lime, aluminum sulfate, and ferric chloride. Biological treatment systems have also been developed which can reduce the effluent P content to less than 1 mg/L (Levin, 1972).

While the introduction of excess phosphate must be avoided in fresh water systems, the addition of phosphate to agricultural land is often deemed necessary. Additions are usually made by applying phosphate fertilizers. Irrigation of agricultural land with wastewater to increase the nutrients in the soil is an old practice and is attractive for minimizing the use of expensive fertilizers as well as being a highly efficient reuse of wastewater (Hyde, 1976). However, the successful use of wastewater on crop lands must be tempered by a knowledge of the toxic metal, pathogenic bacterial and viral components, toxic organic residues, and other hazardous constituents of the wastewater (Schmidt, et al., 1975; Iskandar, 1975; Anderson, 1978; Larkin, et al., 1978; Brown, 1978). Crops grown on land irrigated with wastewater may, therefore, not be suitable either for human consumption or as forage for livestock. Toxic materials may also prevent proper growth of plants. The effects of hazardous materials in wastewater vary widely with the particular wastewater to be disposed, method of pretreatment, application, and the management of the disposal site (Olsen and Guinn, 1978).

Statement of the Problem

The motivation for this research project arose from an inability to explain some specific effects on the removal of phosphate from wastewater. Two soils with widely divergent phosphate sorbing properties were selected for study based on results published by workers at the Cold Regions Research and Engineering Laboratories of the U.S. Army Corps of Engineers at Hanover, NH (Iskandar, et al., 1976).

A wastewater land treatment site in Manteca, California was found to be leaking phosphate. Soil solution concentrations of up to 9.9 mg/L P were found at a depth of 1.6 m for samples collected with a suction lysimeter in the Tujunga coarse sandy loam at the treatment site. Background levels of P in the soil solution of a control field not used for wastewater treatment were also elevated; approximately 1 mg/L P as phosphate. No significant contamination of the groundwater was observed but the potential for such contamination was high (Murrmann and Iskandar, 1976). The other soil, Charlton Silt Loam, is a typical New Hampshire soil that has been shown to sorb large amounts of phosphate in a prototype land treatment system (Iskandar, et al., 1976).

The phosphate sorbing properties of each soil were examined in detail, including studies on the sorption capacities, kinetics of adsorption, desorption and exchangeability of sorbed phosphate, influence of various

physical and chemical soil properties, and pH effects. By comparing these two contrasting soils, it was hoped that the variables that control differences in their behavior could be determined. The ultimate goal was to contribute to the development of predictive models which will permit intelligent and efficient management of wastewater land treatment sites.

CHAPTER II

SOIL - PHOSPHATE BEHAVIOR: A REVIEW OF THE LITERATURE

The literature covering investigations of phosphate sorption behavior of soils is extensive. However, while some very general conclusions may be drawn from the reported work, there is little consensus on the particulars of phosphate sorption behavior. In fact, the apparently contradictory conclusions reached among the workers in this field lead to confusion which is enhanced by the large number of publications.

In examining the work performed in the area of soil phosphate sorption, and in soil science in general, one must be constantly aware of the inherent complexity of the topic. The physical, chemical, and biological nature of a soil system vary continuously among locations. A sample removed from a single small area is itself a heterogeneous system containing materials having diverse properties. The wide distribution of particle sizes and the heterogeneous nature of the soil cause difficulties in obtaining truly "representative" samples. Furthermore, many of the methods employed to characterize soils produce information defined

more by the procedure used than by any sharp distinction implied by a simple label.

As a result of these problems, a review of the literature cannot be expected to yield a precise understanding of the problem. Each group of workers has chosen to examine a particular soil or group of soils using a particular set of procedures. Consequently, results reported by different investigators cannot always be directly compared. All interpretations of the findings must be tempered with the knowledge that such a variety of materials and methods are used. Nonetheless, a general understanding of the problem can be gained by a careful examination of past and continuing work in soil behavior.

Soil Phosphate

Soils generally contain relatively low amounts of phosphate, ranging from 0.01% to 0.25% (Bolt and Bruggenwert, 1976). The levels present in soils vary considerably due to the presence of phosphate minerals, fertilization practices in farming areas, past leaching of phosphate compounds, and additions of plant residues (Black, 1968).

Soil phosphorus occurs naturally almost exclusively as orthophosphate, PO_4^{3-} , found in both organic and inorganic forms. The relative proportion of phosphate in these two general forms depends on the organic matter

content and source of phosphate. The organic phosphate content of surface soils varies from 0.3% to 95% of the total phosphate present. The organic forms probably include nucleic acids, phospholipids, inositol phosphate, and many other specific forms. Due to the difficulties of isolation and identification, the specific nature of soil organic phosphates remains unresolved. The sources of these organic compounds are often degradation of plant and animal material, but some microorganisms also produce organic phosphates as waste material, particularly inositol phosphates.

The inorganic forms of phosphate have been studied in detail, particularly as to their mineralogical nature. Apatite $[\text{Ca}_{10}\text{X}_2(\text{PO}_4)_2]$, $\text{X} = \text{F}, \text{Cl}, \text{OH}$, vivianite $[\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}]$, and wavelite $[\text{Al}_8(\text{OH})_3(\text{PO}_4)_2 \cdot 5 \text{H}_2\text{O}]$ are the predominant phosphate minerals present in soils. However, phosphate not present as discrete minerals is most directly involved in the water - soil interactions. The exact natures of these compounds are not known but a variety of iron, aluminum, and calcium phosphates are indicated (Lindsey, et al., 1962). Amorphous "hydrous oxides" have been extensively used as model systems to study phosphate adsorption properties of soils (Ryden, et al., 1977a; Parfitt, et al., 1975; Hsu and Rennie, 1962).

The irreversible binding of phosphorus by soils was first investigated to examine the deactivation of phosphate fertilizers applied to farmland (Lindsey, et al., 1962; Murrmann and Peech, 1968). Recent work has emphasized the study of phosphate sorption capacities and mechanisms for the handling of phosphate waste. The action of sediments in reducing the phosphate content of lake water has also been extensively examined (Syers, et al., 1973; Li, et al., 1972). Many parallels can certainly be drawn between sediments and soils but one must be conscious of the chemical changes which will occur with a soil kept in waterlogged conditions.

Adsorption Models

The practical goal of most phosphate sorption studies is to aid in the determination of the phosphate sorption capacity of a particular soil. Ideally, a relatively simple mathematical model may be found which accurately indicates the rates and absolute amounts of phosphate which a soil can sorb.

Simple adsorption models have been used for many years in evaluating chemical interactions in soil systems. The Langmuir equation and variations of it are often used to predict sorption capacities of soils. However, these models appear adequate for only a few soils within a limited phosphate concentration range. Failure of the Langmuir

equation arises from the assumptions inherent in its development. First of all, it was developed as an intentionally simplistic model for gas - solid interaction and assumes ideal gas behavior, an adsorbed monolayer, surface homogeneity of the solid, non - interaction of adsorbed materials, and no lateral movement of adsorbates (Daniels and Alberty, 1966). Certainly none of these assumptions are valid for the interaction of a dissolved ionic species with the surface of a clay particle.

The empirical Freundlich equation, also a gas adsorption model, which allows for heterogeneous reactive sites on the solid surface, has also met with limited success, and in any case cannot be used to predict a maximum of adsorbed material.

More complex models of phosphorus sorption have been proposed, particularly addressing the kinetics of the sorption process and predictions of phosphorus movement through the soil (Enfield and Shew, 1975; Enfield, 1974; Novak and Adriano, 1975; Enfield, et al., 1976; Enfield, 1978). Most of these models use predicted phosphate sorption maxima derived from empirical data along with factors of particle size, soil bulk density, velocity of migration of solution, and various other factors to predict phosphate movement. However, while a few models include terms designating the amount of native mineral phosphate and mineral aluminum and iron present, an exhaustive treatment

of possible reaction products of phosphate and substances found in both the soil and soil solution has not been presented. Treatments that ignore possible desorption of native and/or previously sorbed phosphate have been shown to predict soil behavior inaccurately (Harter and Baker, 1977). An exhaustive treatment of all factors is prohibitively complex and may be unnecessary. Many of the models already presented in the literature have yet to be tested in the laboratory and/or in the field and one or more may yet prove successful (Enfield, 1978). However, variables such as pH, Eh, ionic strength, and the inhomogeneities of soil and wastewater must be carefully treated in any model that will meet with general success.

While all models have questionable application to field conditions, the Langmuir isotherm equation still finds very wide use in studying phosphate sorption behavior in the laboratory. This extensive use is due to the fact that it allows simple calculation of sorption maxima and relative sorption energies, both of which aid greatly in evaluating the sorption process. The examination of these parameters allows informed statements to be made on the mechanism or multiple mechanisms involved in the sorption process (Ryden, et al., 1977a).

Factors Affecting Phosphate Sorption

If phosphate sorption consisted of a simple adsorption process on the surface of the soil particles, the behavior would depend primarily on a few physical parameters; particle size distribution, surface area, porosity of the particles, surface charge, and fluid dynamics defining flow around the particles. The sorption models described above deal primarily with just these effects and generally fail to follow empirical studies. Obviously, the sorption process is not simple and consists of a complex interplay of adsorption, chemisorption, ligand exchange, crystal growth, and precipitation. Thus, chemical interaction of dissolved phosphate with the surface of soil particles plays a major role in sorption behavior.

Reactive Materials

Deactivation of phosphate fertilizers has long been credited to the formation of phosphate compounds rendering phosphate unavailable to plants (Lindsey, et al., 1962). Identification of the exact compounds formed is of interest both in considering the problems of fertilization and in studying intentional phosphate retention by soils. Lindsey, et al. (1962) equilibrated saturated solutions of several phosphate fertilizers with soils and identified the precipitation products formed over extended periods of time. They found a large variety of calcium, aluminum, iron and

manganese phosphate compounds, some indistinguishable from phosphate minerals, (hydroxyapatite, strengite), as well as other phosphate compounds and unidentifiable mixtures. Murrmann and Peech (1968) studied soils which were fertilized and limed five years before the initiation of the study. By examining the solubility of soil phosphate and soil calcium, they found that the long term reaction products of phosphate in soils consisted of the apatite series, with fluoroapatite as the ultimate product.

Various workers have shown that phosphate sorption capacities of soils can be correlated to the concentration of various materials in the soil. Aluminum, iron, calcium, and organic matter are generally recognized as the materials establishing overall phosphate sorbing properties of a soil. Extractable iron and aluminum have been very closely correlated with phosphate sorption abilities of soils (Vijayachandran and Harter, 1975; Ballard and Fiskell, 1974). The iron and aluminum content of soil, determined by a dithionite - citrate - bicarbonate extraction (Mehra and Jackson, 1960) that reportedly removes amorphous free iron oxides and associated alumina, appears to be the factor most closely correlated to phosphate sorption capacities (Syers, et al., 1971). Still, the relative importance of iron and aluminum compounds is a topic of much debate. It has been suggested that amorphous aluminosilicates are more active per unit weight than iron compounds (Syers, et al 1971; Vijayachandran and Harter, 1975).

Calcium has been found to play an important role in phosphate binding, particularly in calcareous soils. Due to the low solubility of calcium phosphate compounds, it is thought that a rapid adsorption of phosphate onto the calcium compound surface is followed by a precipitation and crystallization process (Mattingly, 1975).

It has been suggested that an equilibrium exists among phosphate - containing compounds such that the least soluble forms will tend to be the ultimate products of sorption, although equilibration may be slow (MacKensie, 1962). This explains the fact that phosphate sorption ability of many soils appears to be self - regenerating to a large degree. The more soluble forms of phosphate, which generally are thought to be the forms produced by rapid sorption, will be altered slowly to less soluble forms while also regenerating the original material for rapid sorption (Hsu and Rennie, 1962; MacKensie, 1962). However, this redistribution of phosphate occurs very slowly in many soils, while regeneration of rapid sorption sites often occurs rather quickly (Mattingly, 1975). Hsu has suggested that accelerated decomposition of soil may result from sorption of phosphate. This accelerated destruction of mineral structure would make available more surface active materials for sorption, particularly aluminosilicates (Hsu, 1965). The long term effect of this process may be destruction of the suitability of a soil for agricultural use as well as wastewater treatment, although evidence for this is not convincing.

Organic matter has been credited with both increasing and decreasing the amount of P sorbed. Weir and Soper (1967) found that less phosphate was irreversibly bound in soils to which large amounts of manure were added. They believe that soluble iron and aluminum complexes formed by interaction with the organic material were responsible for the effect. Vijayachandran and Harter (1975) suggested that organic material will enhance phosphate binding by physical adsorption of phosphate on the organic material. Complexation of phosphate with metallo - humics may also play a role in the eventual mineralization of phosphate (Nissenbaum, 1979). On the other hand, Weir and Black (1968) determined that additions of inorganic phosphorus had little effect on the mineralization of organic phosphorus in soils.

pH Effects

The effect of soil solution pH on phosphate sorption processes is debated widely. When a pH effect is recognized, it is usually based on a trend toward lower sorption with an increase in pH. This is generally attributed to a reduction of the charge on the clay surface as it approaches the point of zero charge, generally around pH 8 (Ryden and Syers, 1977a; Madrid and Posner, 1979). Soil pH and effects of pH changes on phosphate sorption vary considerably with different soil types.

By considering the pH effect on the solubility of phosphate minerals, other rationalizations can be made of the observed trends. Variscite and strengite increase in solubility with an increase in pH while the calcium containing phosphate minerals; fluoroapatite, hydroxyapatite, octocalcium phosphate, and dicalcium phosphate hydrate all decrease in solubility with an increase in pH (Weir and Soper, 1962; Lindsey and Moreno, 1960). Thus, it is suggested that iron and aluminum associated phosphate forms will be more stable in acid soils than in alkaline soils, and the opposite effect will apply to the calcium associated phosphate forms. This is supported by the general differences observed between calcareous and non-calcareous soils.

Nur and Bates (1979) reported that phosphate binding in lake sediments reached a minimum at pH 7.33. They found that the minimum fixation for aluminum, iron, and calcium phosphate fractions all occurred at a near neutral pH. This is in apparent contradiction to the trends predicted on the basis of solubility properties of the metal phosphates. The complexed relationship of Eh, pH, and biological activity in sediment systems may cause the observed behavior.

Hsu (1973) commented on the large range of pH values reported as "optimum" for precipitation of iron phosphates in wastewater treatment with pH values ranging from 2.5 to 7.4. He found that the OH^-/Fe concentration ratio in

solution was a more important factor than pH alone at low phosphate concentration levels ($P/Fe \leq 0.8$). The optimum OH-/Fe ratio varied with the particular phosphate concentration. At high phosphate concentrations, the effect of the OH-/Fe ratio was minimal.

The effect of changing the pH of a soil system must also be considered. As the natural pH of the soils is altered, shifts in soil solution equilibria will certainly occur. Alterations in the surface charge of the clays, and other particulates will all affect the manner of phosphate adsorption. A slow increase in soil pH is generally observed at wastewater land treatment sites (Bouwer and Chaney, 1974). Consequently, any detrimental effects of soil pH alteration on phosphate sorbing properties of the soil may decrease the long term use of a disposal site.

Effects of Flooding of Soils; Changes in Eh

Under waterlogged conditions, as may occur with some methods of land treatment of wastewater, major chemical changes can occur in the soil. As the oxygen content of the soil is depleted, the action of sequentially heterotrophic, autotrophic, and obligatory anaerobes will result in the development of reducing conditions in the soil (Gotoh, 1973; Ponnamperna, 1972). The chemical environment of the soil changes dramatically under these conditions with the reduction of Fe (III) to Fe (II), nitrate to ammonia,

sulfate to sulfide, and other conversions. The development of such conditions can dramatically affect phosphate sorption processes. Patrick and co-workers have conducted numerous investigations on the pH, moisture regime, initial phosphate content of the solution, and iron content of the soils (Mahapatra and Patrick, 1969; Patrick and Khalid, 1974). They have reported that the chemical state of iron present in soil is an important factor in phosphate fixation. Fe (III) generally binds phosphate in less soluble forms than does Fe (II) (Patrick and Khalid, 1974). Since large quantities of iron may be reduced under waterlogged conditions in a soil (Asami, 1970; Ponnampereuma, 1972; Turner and Patrick, 1968), phosphate sorption may be drastically reduced.

The effects of aerobic versus anaerobic conditions on phosphate sorption behavior are complex. Patrick and Khalid (1974) found that with high initial concentrations of phosphate, a reducing atmosphere enhances phosphate adsorption relative to the same soil under oxidized conditions. At low P concentrations, the opposite is true. While the solubilities of ferrous phosphates are markedly higher than ferric phosphates, the much greater surface area of the reduced hydrous iron oxides as compared to oxidized forms may result in an increased sorption capacity and rate of sorption.

Mahaprata and Patrick (1969) reported that for phosphate initially associated with the soil, waterlogging resulted in increased insoluble aluminum and iron phosphate content at the expense of soluble phosphate. The calcium phosphate content of the soil did not change substantially upon waterlogging.

Under long term, highly reduced conditions, actual destruction of clay structure occurs (Brinkman, 1970). The resulting soil is characterized by very low cation exchange capacity and low pH, which in turn leads to high mobility of previously bound substances. The soil becomes unsuitable for plant growth as well as wastewater treatment.

The complex effects of the development of anaerobic conditions in a soil system will continue to be of interest to soil scientists. Difficulties in developing good experimental procedures for working with soil systems under reduced conditions have resulted in the lack of a completely consistent picture of the sometimes dramatic effects involved.

Exchangeability of Sorbed Phosphate

If the sorption process is a simple physical adsorption process, it should be fully reversible. Phosphate thus adsorbed should be exchangeable with solution phosphate and should desorb if the solution concentration drops below the equilibrium value. Exchangeability of sorbed phosphate

indicates the degree of reversibility and thus the stability of the materials formed. Use of radioactive phosphorus allows one to follow adsorption and exchange reactions in soils.

Weir and Soper (1962) found that phosphate associated with aluminum in the soil was readily exchangeable. As the calcium content of the soil increased, the amount of exchangeable phosphate decreased. Iron associated phosphate showed intermediate behavior. Their findings appear to support the idea of low - solubility calcium products being the ultimate forms of sorbed phosphate.

Mattingly (1975) distinguished several forms of phosphate in soils based on the degree of exchangeability exhibited. He also showed that after aging for periods of 1 to 5 months following equilibration with phosphate solutions, the ratio of exchangeable phosphate to sorbed phosphate was almost constant, indicating the establishment of an equilibrium.

Barrow and Shaw (1975) found that the amount of isotopically exchangeable phosphate increased proportionally with the amount of P sorbed but decreased with increasing equilibration time. This again indicates that a slow conversion process occurs among phosphate forms after initial sorption. Changes in pH did not affect the exchangeability properties in a continuous manner. Competitive pH effects on the solubilities of various

phosphate compounds present explain this complex behavior. Ryden and Syers (1977d) observed similar effects on the exchangeability of phosphates in soils.

Mechanisms of Sorption

Many different mechanisms for phosphate sorption on soil particles have been proposed, but as with much of the reported work in this field, there is little consistency in views. Anion exchange, simple adsorption, chemisorption, ligand exchange and many other processes have been postulated as contributing to the overall sorption process. It is quite possible that all of these processes are involved.

Parfitt et al. (1975) used infrared spectroscopic techniques to observe changes in the surface structure of iron oxides sorbing phosphate. They concluded that phosphate formed a strongly bonded binuclear complex with Fe (III) ions on the surface of hydrous iron oxide gels. While the spectral properties of minerals examined obscured the results, a similar reaction was assumed to occur with clay particles.

In Langmuir isotherm studies, Hsu and Rennie (1962) found that phosphate fixation appears to follow true adsorption behavior in amorphous aluminum hydroxide. They reported that phosphate is primarily sorbed on the surface of the aluminum hydroxide since significant amounts were

desorbed upon reequilibration. However, a precipitation reaction may follow the initial adsorption, forming hydroxyl aluminum phosphates under neutral or slightly acidic conditions (Hsu, 1965). At this point, Hsu believes decomposition of the aluminum hydroxide occurs, exposing fresh surface for a new initial adsorption step. Because of this competitive precipitation and decomposition behavior, actual mineralization of the sorbed phosphate may never occur in nature.

Barrow and Shaw (1975b) proposed that soil phosphate exists in three "compartments" in successive equilibrium with each other. The first compartment includes labile phosphate that is exchangeable with solution phosphate. The second compartment, in equilibrium with both the first and third, contains bound phosphate, probably formed through ligand exchange with hydroxyl groups on the hydrous oxide surfaces. The third compartment, in equilibrium with the second, but not with the labile phosphate, contains tightly bound forms, possibly involving double linkage to the oxide surface. Barrow has attempted to quantify temperature effects with sorption behavior as well as studying the effects of other experimental conditions such as soil:solution ratios and vigor of mixing (Barrow, 1975b; 1979c).

Ryden et al. (1977a) reported that three distinct sorption regions were consistently found for the Langmuir isotherm studies of different soil types and for synthetic hydrous iron oxide. At low P concentration, the dominant mechanism is a substitution of phosphate for protonated hydroxyl groups on the hydrous iron oxide surface. This chemisorption reaction is pH dependent since the hydroxyl groups of the iron oxide must be protonated. The second mechanism involves a substitution of phosphate for unprotonated hydroxyl groups on the hydrous oxide. This reaction becomes the dominant form of sorption when the protonated reactive sites are saturated. Thus, while the second mechanism is independent of pH, its degree of contribution to the overall sorption process is dependent on the predominance of the first, pH dependent mechanism. Finally as all hydroxyl sites on the hydrous iron oxide are saturated, a third mechanism, involving a weak, more physical sorption onto the surface of the hydrous oxide becomes dominant. This more physically sorbed phosphate is much more susceptible to isotope exchange than the chemisorbed phosphate. Under some circumstances, the more physically sorbed phosphate can be completely desorbed (Ryden, et al., 1977e; Ryden and Syers, 1977c).

Ryden, Syers, and their coworkers have rationalized the effect of ionic strength and cations (Ryden and Syers, 1975; Ryden, et al., 1977e), kinetic studies (McLaughlin, et al., 1977; Ryden, et al., 1977b), desorption and

exchange (McLaughlin and Syers, 1978; Ryden and Syers, 1977d), and availability of phosphate in soils (Ryden and Syers, 1977c) to this three process mechanism. Thus, this mechanism is the most elegant and complete description of phosphate sorption behavior of soils to emerge in the literature to this time.

CHAPTER III

SOIL AND EFFLUENT CHARACTERIZATION

Introduction

The soils to be studied were chosen on the basis of previous work conducted by the Cold Regions Research and Engineering Laboratories (CRREL) at Hanover, NH, as described in the statement of the problem. The two soils, Tujunga loamy coarse sand from the wastewater treatment site located at Manteca, CA, and Charlton silt loam from the prototype land treatment facility at CRREL, had exhibited vastly different phosphate binding. Quite high soil solution phosphate concentrations were found at the Manteca site. Samples from treatment fields actually desorbed phosphate when equilibrated with solution containing less than 8 $\mu\text{g}/\text{mL}$ of P (Iskandar and Syers, 1980). The Tujunga soil used in these studies was removed from a control field located adjacent to the fields used for disposal of wastewater. This control field has never received any wastewater and is thought also to be free from any phosphate fertilizers.

At the beginning of this project, the decision was made that the sorption behavior would be examined using effluent from a sewage treatment system rather than an inorganic salt solution. While this increased the complexity of the system studied, actual treatment conditions were better approximated.

Very little previous work has been reported using wastewater except for field studies and work with soil column systems (Sawhney and Hill, 1975). Van Riemsdijk, et al. (1977) used an "inorganic synthetic sewage water medium" in sorption studies. This medium contained inorganic salts in concentrations similar to those of typical wastewater. They reported that this synthetic sewage water did not mimic some of the characteristics of actual sewage water, including buffering capacities and carbon dioxide saturation. Also, the complete absence of organic material and particulates eliminated the influences of these materials which are typically found in wastewater. Many possible differences in behavior of soils equilibrated with wastewater and inorganic solutions can be expected. Ionic strength effects have been clearly shown to influence the sorption behavior (Ryden, et al., 1977a; Barrow, 1979). The formation of organic complexes of phosphate and/or iron and aluminum may significantly affect the observed behavior.

Selection of the domestic wastewater used in this project was entirely a matter of availability and convenience. While the measured characteristics of the wastewater all fall within the normal ranges reported, implication that this sample is entirely "typical" is not intended.

Experimental Procedures

Soils

The entire available supply of each soil (approximately 1 kilogram in both cases) was air dried at room temperature and passed through a sieve to remove any particles greater than 2 mm in diameter. Each sieved soil was stored in a single sample bag. For the studies conducted before June, 1979, samples were removed from these bags at random as needed. In June, 1979, the entire remaining supply of each soil was subdivided into 10.00 gram samples using a Fisher brand Riffle Sampler (Cat. No. 4-940) and a Soil Test brand Precision Sample Splitter (Cat.No. C1-242B). These samples were stored in polystyrene sample containers and chosen at random for all further experiments.

Soil particle size distribution was determined using a sedimentation method after wet sieving through a 47 μm sieve (300 mesh). The readily oxidizable organic carbon of the

soils was determined by oxidation with potassium dichromate in concentrated sulfuric acid, followed by titration of excess dichromate with 0.5 M ferrous ammonium sulfate solution (Gaudette, 1974).

Free iron oxide and associated alumina content of each soil was determined using the dithionite - citrate - bicarbonate extraction procedure of Mehra and Jackson (1960) with three successive treatments with dithionite as modified by Iskandar (personal communication). Extractable calcium content was determined by heating 1 gram of soil with 40 mL of 0.5 M HCl at 100°C for 1 hour. All extractions were performed in triplicate. Extracts were analyzed using a Varian-Techtron atomic absorption spectrometer equivalent to Model AA6, with a DI-30 digital integrator. The determinations were made as follows: iron by atomic absorption using an air-acetylene flame; aluminum by atomic emission using a fuel rich nitrous oxide-acetylene flame; calcium by atomic absorption using an air-acetylene flame in the presence of 0.1% La to eliminate phosphate interference. Accuracy of the analyses was verified using the method of standard additions.

Effluent

The effluent used in experiments previous to June, 1979, was collected on December 7, 1977 at the Durham, NH sewage treatment plant, a secondary treatment facility. The

concentration of filterable orthophosphate was 4.0 mg/L (ppm P as PO_4^{3-}) and the pH of the effluent was 6.8. The entire supply of effluent was frozen shortly after collection and stored at -25°C until just before use. To assure homogeneity and to promote uniform size of particulate matter from sample to sample, individual portions of effluent were thoroughly mixed in an electric blender immediately before use.

The effluent used in the studies after June, 1979, was collected from the Durham sewage treatment plant on July 3, 1979. The filterable orthophosphate ($< 0.45 \mu\text{m}$) content was 2.40 mg/L P as phosphate, the total P was 3.80 mg/L, and the pH was 6.2. This effluent batch was stored and handled as described above.

Spectrophotometric determinations of orthophosphate were performed using a Technicon AutoAnalyzer II, following the procedure recommended by the manufacturer (Murphy and Riley, 1962). Measurements were made on untreated filtrate ($< 0.45 \mu\text{m}$) as well as filtrate subjected to persulfate digestions (Standard Methods, 1975), with no difference in P concentration detected. Total P was measured using the persulfate digestion of unfiltered effluent. Dissolved organic carbon content of the effluent was determined using a Sybron/Barnstead Photochem Organic Carbon Analyzer after filtering the sample through a $0.45 \mu\text{m}$ nitrocellulose filter. The filterable residue, total residue, total fixed

residue, and total volatile residue were found as designated in Standard Methods.

To improve consistency among effluent samples, a gallon was thawed, poisoned with 40 mg/L mercuric chloride and subdivided into 100 mL samples which were stored in separate polypropylene containers for later use in sorption studies. These samples were refrozen until just before use at which time they were thawed in a lukewarm (approximately 30° - 35°C) water bath. This procedure was adopted to minimize any effects of bacterial action and chemical processes which might alter the composition of the effluent.

In normal land treatment of wastewater, effluent would contain particulate material. Consequently, we wished to perform sorption studies using unfiltered effluent. However, sorption studies require filtration to separate soil from solution prior to analysis. This process unavoidably removes effluent particulates as well as soil. Therefore, it became necessary to determine if effluent particulates could influence apparent sorption behavior by interactions with P-32 or by chemical changes associated with pH adjustments.

For these reasons, phosphorus distribution and behavior in the effluent were examined. Aliquots of effluent (100 mL), either poisoned with 40 mg/L mercuric chloride or non-poisoned, were adjusted to pH 5.0, 6.5, or 8.0 and maintained at that pH with gentle stirring for one hour.

One milliliter of each solution was filtered through a 0.45 um nitrocellulose filter and diluted to an appropriate concentration for analysis. Total phosphate content of each solution was determined following a persulfate digestion on a second 1 mL sample. Resulting digests were filtered and diluted for analysis.

The equilibration of P-32 tracer within the effluent alone was also examined. Samples (100 mL) of both poisoned and non-poisoned effluent were again adjusted to pH 5.0, 6.5, and 8.0, and a small amount of carrier free P-32 as phosphoric acid (New England Nuclear) was added. After an equilibration period of one hour, a 1 mL sample was filtered, and the filtrate dried in a cupped planchet. A total of 10 mL of the solution was passed through another filter, which was then placed in a cupped planchet, dissolved in acetone and dried, leaving a thin film to minimize self - absorption effects in counting. The radioactivity of these samples was determined using an end-window Geiger-Muller detector connected to a standard scaler and associated electronics. The distribution of P-32 was also examined in effluent samples to which 50 mg/L P as phosphate was added to see if increasing the phosphate levels in the effluent would cause an increased exchange between the dissolved and condensed forms of phosphate.

RESULTS AND DISCUSSION

Soil Particle Size Distribution

The Tujunga soil contains much higher amounts of sand than the Charlton soil (Table 1). The relative coarseness of the Tujunga soil suggests that applied effluent should percolate through the soil at a rather rapid rate, thereby lowering the residence time for chemical removal of phosphate by the soil. Correspondingly, there is a greater fraction of smaller soil particles in the Charlton soil. The proportion of silt is substantially greater in the Charlton soil. While both soils are relatively low in clay content, there is a significantly greater percentage in the Charlton soil. Due to the much greater surface area and amount of reactive material associated with the small particles, the silt and clay fractions account for the major proportion of sorption occurring in the soil. On this basis alone, we would expect the Charlton soil to have significantly greater sorption capacity than the Tujunga soil. However, the particle size differences are inadequate to explain the dramatic P sorption differences. Particle size analyses also give no hint of the chemical reactions associated with phosphate sorption.

Table 1. Particle Size Distribution.

<u>Size Fraction</u>	<u>% by Weight</u>	
	<u>Tujunga</u>	<u>Charlton</u>
Sand >47 μm	86.1%	58.5%
Silt 47 μm - 2 μm	11.6%	38.4%
Clay <2 μm	2.3%	3.1%

Soil Reactive Compounds and Organic Carbon Content

The free iron oxide and associated alumina concentrations in the Charlton soil were, respectively, four and ten times larger than in the Tujunga soil (Table 2). These large differences can be partially explained by the lower amounts of silt and clay in the Tujunga soil, but they also indicate a difference in overall chemical makeup. The HCl extractable calcium content of the Tujunga soil is somewhat higher than the Charlton soil, indicating a much greater proportion of calcium with respect to other reactive species in the Tujunga soil. Thus, calcium compounds may have a greater influence on phosphate binding behavior of the Tujunga soil.

The oxidizable organic carbon content of the soils also differ greatly, with the Charlton soil containing four times the organic carbon of the Tujunga soil. This difference may also have some effect on the sorption behavior of the soils, but the carbon concentrations cannot be considered to be high in either soil.

Native Phosphate Distribution

The identification of the metals with which phosphate is associated in soils is a major problem in analysis. Various procedures have been used to extract the different phosphate fractions selectively. The procedure of Chang and Jackson (1957) and modifications of their original procedure

Table 2. Extractable Free Iron Oxide and Associated Alumina, Calcium, and Organic Carbon Content of the Soils.

	<u>Tujunga</u>	<u>Charlton</u>
%Fe ₂ O ₃	0.39%	1.6%
%Al ₂ O ₃	0.14%	1.6%
Ca	115 µg/g	90 µg/g
Organic C	0.54%	2.1%

are most commonly used to identify the associated forms of phosphate in soils. According to the Chang and Jackson procedure, phosphate is extracted as the nominally soluble fraction (1 M ammonium chloride extract), aluminum associated fraction (pH 7.0, 0.5 M ammonium fluoride), iron associated phosphate and organic phosphate (0.1 M sodium hydroxide), calcium associated phosphate (0.25 M sulfuric acid), and "occluded" phosphates (0.3 M sodium citrate and sodium dithionite). However, all such fractionation estimates must be interpreted cautiously because sharp distinctions among fractions are not achieved. While each fraction contains materials other than the labels imply, the procedure does provide a means to compare the relative abundance of phosphorus forms in soils (Ballaux and Peaslee, 1975; Barrow and Shaw, 1971; Williams, et al., 1967).

Despite the empirical nature of the procedures, the results of the Chang and Jackson methodology show large differences between the two soils (Table 3). In the Charlton soil, the phosphate is primarily associated with "aluminum and iron fractions", while only a small fraction of the phosphate in the Tujungua soil is similarly associated. Even allowing for the lack of specificity in the Chang and Jackson extraction procedure, the differences in the phosphate forms present are drastic enough to permit the prediction that phosphate sorption in the two soils might be quite different. Also, while the Charlton soil exhibits a greater capacity to adsorb phosphates, it

Table 3. Native Phosphorus Distribution According
to the Procedure of Chang and Jackson (1957).

<u>Extractant</u>	<u>Charlton</u>	<u>Tujunga</u>
	$\mu\text{g/g P as PO}_4^{3-}$	$\mu\text{g/g P as PO}_4^{3-}$
1 M NH_4Cl (Soluble P)	0	5
0.5 M NH_4F (Al-associated P)	301	58
0.1 M NaOH (Fe-associated P)	167	20
0.25 M H_2SO_4 (Ca-associated P)	90	390
Total P	558	473

contains about 100 $\mu\text{g/g}$ more native phosphate than the Tujung soil.

Effluent Characteristics

The measured characteristics of the effluent are presented in Table 4. All of these values are typical of effluents, though the phosphate level is low-normal (Bouwer and Chaney, 1974). Thus, the effluent used in these studies is fairly typical of effluent encountered in land treatment facilities.

Effluent Phosphorus Content and Reactivity

No significant changes were observed for the distribution of orthophosphate between soluble and particulate forms in the effluent at pH 5.0, 6.5, and 8.0 after an equilibration time of 1 hour. The natural pH of the effluent at the time of collection was 6.2. The addition of 40 mg/L of mercuric chloride also had no effect on the phosphate distribution. Persulfate digestion of the filtered dissolved orthophosphate samples resulted in no higher detectable levels of phosphate than obtained without digestion. This means that all of the condensed phosphate is associated with the particulate matter of the effluent.

The degree of isotope exchange between the filterable phosphate in the effluent and the particulate forms was small but significantly affected by pH changes. In all

Table 4. Effluent Characteristics.

Dissolved Organic Carbon	14.7	mg/l
Total Residue	407	mg/l
Total Particulate Matter	60	mg/l
Total Filterable Residue	347	mg/l
Total Fixed Residue	280	mg/l
Total Volatile Residue	127	mg/l
Filterable Orthophosphate	2.40	mg/l
Total Phosphate	3.80	mg/l
pH	6.2	

cases of effluent equilibrated at pH 5.0 and 6.5, approximately 1% of the radioactive phosphate was associated with the particulate matter after 1 hour of equilibration. Poisoning of the effluent had no further effect at these pH values. However, at pH 8.0 and the natural effluent phosphate level (2.40 mg/L filterable P), 2.5% of the P-32 was found in the particulate phase. Again, no significant differences between the poisoned and non-poisoned samples were observed. Where the effluent phosphate level was raised to 50 mg/L P before P-32 equilibration, both pH 8.0 and poisoning altered the redistribution of the tracer. In poisoned effluent at pH 8.0, 3.4% of the radiotracer was in the particulate fraction, while in non-poisoned samples, the amount increased to 5.5%. Apparently, at pH 8.0, isotope exchange processes between the dissolved and condensed forms in the effluent become significant. This exchange is further enhanced by microbial action.

While these findings indicate the existence of a small influence by effluent particulate matter on P-32 distribution at a solution pH of 8.0, impact on adsorption/desorption studies with soils would be small if not negligible. This is especially true at natural phosphate levels.

CHAPTER IV

ADSORPTION ISOTHERM AND ISOTOPE EXCHANGE STUDIES

Introduction

Measurement of adsorption isotherms is the method most commonly employed for the study of soil - phosphate sorption. While a great deal of basic information can be derived from isotherms (See Chapter 2), they also provide a simple means to compare two or more soils.

Conventional equilibrium isotherms are usually constructed from a large amount of data in order to define the isotherm at low solution concentrations. In this research, isotherms were developed to provide information relevant to the discussion of the kinetic studies presented in the next chapter. As such, conditions for the isotherm studies were kept as similar as possible to the conditions used in the kinetic studies. The lower limit of solution concentration was established by the effluent phosphate concentration. Thus, a well defined isotherm for very low solution concentrations was not possible. However

the conditions do effectively mimic those expected in land treatment systems.

Isotope exchange between the effluent particles and solution phosphate is enhanced when the phosphate content of the effluent is increased, as is discussed in Chapter 3. Thus competitive effects will be observed in the isotope exchange measurements made in the following study.

Despite these problems, the equilibrium isotherms were conducted using effluent with phosphate added as needed. This procedure better reflects the actual treatment of wastewater by soil application (Iskandar and Syers, 1980). Due to the problems of using effluent in isotherm studies, these isotherms should not be regarded as detailed evaluations of the characteristics of the soils. However, the studies are sufficiently detailed to allow comparison of the sorption capacities and amounts of exchangeable phosphate present after sorption by the two soils.

Experimental Procedures

Ten gram soil samples were equilibrated with 100 mL samples of effluent poisoned with 40 mg/L mercuric chloride. The natural effluent phosphate concentration of 2.4 mg/L P established the lower limit of the concentrations studied since it was necessary to conduct all equilibrations in effluent. For subsequent equilibrations, sufficient phosphate was added to the effluent to raise the

concentration by 25, 50, 65, 85, and 100 mg P/L for the suspensions with the Charlton soil. Additions of 15, 35, 50, 75, and 100 mg/L were used for the Tujunga soil trials. The difference in choice of initial solution concentrations for the two soils was based on the difference in their sorption behavior. The features of the isotherms for each soil were better established with the set of data obtained using these initial concentrations.

The pH of resulting suspensions was adjusted and maintained at 5.0, 6.5, or 8.0 by the addition of HCl or NaOH solutions as needed. A Corning Model 7 pH meter fitted with a Corning Cat. No. 476051 rugged duty combination pH electrode was used to monitor the pH of the suspensions. Equilibration of each soil at each of the initial solution concentrations was studied at each of the three pH's. All of the suspensions were agitated on a platform shaker throughout the equilibration time except during pH adjustment and sampling.

After shaking periods of 24, 48, 72, and 96 hours, representative samples of approximately 1.5 mL were removed from the suspensions and filtered through 0.45 μ m nitrocellulose filters. A 1.0 mL aliquot of filtrate was immediately diluted to an appropriate concentration for spectrophotometric phosphate analysis using the Technicon AutoAnalyzer as discussed in the initial studies of the effluent. The resulting solutions were stored in acid

washed polypropylene bottles at 2°C until analysis was performed.

After 96 hours of equilibration, carrier free P-32 as phosphoric acid (New England Nuclear) was added to provide an activity of approximately 10000 cpm/mL of filtered solution. Shaking of the suspensions was continued for another 8 hours. At this time, samples of the suspensions were removed, filtered, and a 1 mL aliquot of filtrate dried in a cupped planchet over low heat. The radioactivity of these samples were determined using a Geiger - Muller detector as before.

Results and Discussion

The isotherms for both soils at all pH's for a 96 hour equilibration are presented in Figure 1. The dramatic difference in sorption capacity between the Charlton and Tujungsa soils is immediately apparent. Complete data sets for the Charlton and Tujungsa soil adsorption isotherms are presented in Appendices A and B respectively.

Note that the suspensions have not reached equilibrium after 96 hours but approach to equilibrium is sufficient to allow examination of sorption capacity and exchange behavior. The Charlton soil sorbs in excess of 900 ug P/g while maintaining a solution concentration of less than 10 mg/L with pH 5.0 suspension (Further discussion of pH effects follows). On the other hand, the Tujungsa soil

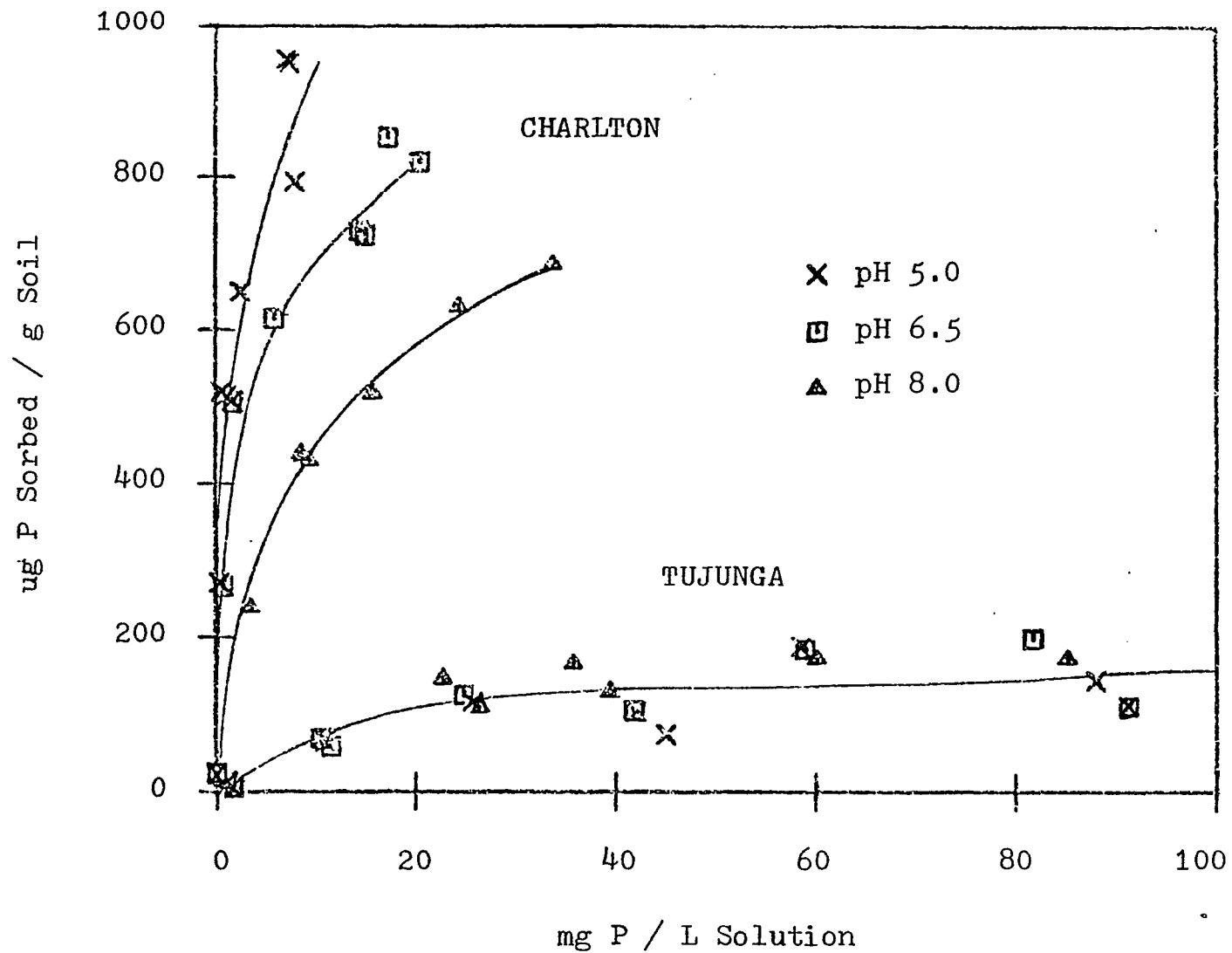


Figure 1. Phosphate Adsorption Isotherms for Charlton Silt Loam and Tujunga Coarse Sandy Loam, 96 Hour Equilibration.

appears to reach a sorption maximum of approximately 150 ug P/g soil. With the natural phosphate level of the effluent, the lowest concentration used for these isotherms, about one-half of the phosphate remains in solution after 96 hours of equilibration with Tujunga soil. These findings verify the very low phosphate sorbing capacity of the Tujunga soil (Murrmann and Iskandar, 1976; Iskandar and Syers, 1980).

Charlton Soil Sorption Isotherms

Figures 2a-d present the isotherms constructed from the 24, 48, 72, and 96 hour data. While minor increases in sorption continue after the first 24 hours of equilibration, the most apparent effect of time is improved resolution of the pH effects. Solution pH has a marked effect on the amount of phosphate sorbed by Charlton soil. Increase in pH from 5.0 to 8.0 results in a steady decrease in the sorption of phosphate at all concentrations. According to Ryden, et al., (1977a), P is sorbed predominantly as physically sorbed phosphate when the equilibrium solution concentration is greater than 1 mg/L, as it is for most of these solutions. Surface charge will play a significant role in more physical sorption. As pH of the suspension increases, there will be a lower overall surface charge on the soil particles since fewer hydroxyl sites will be protonated than at an acidic pH.

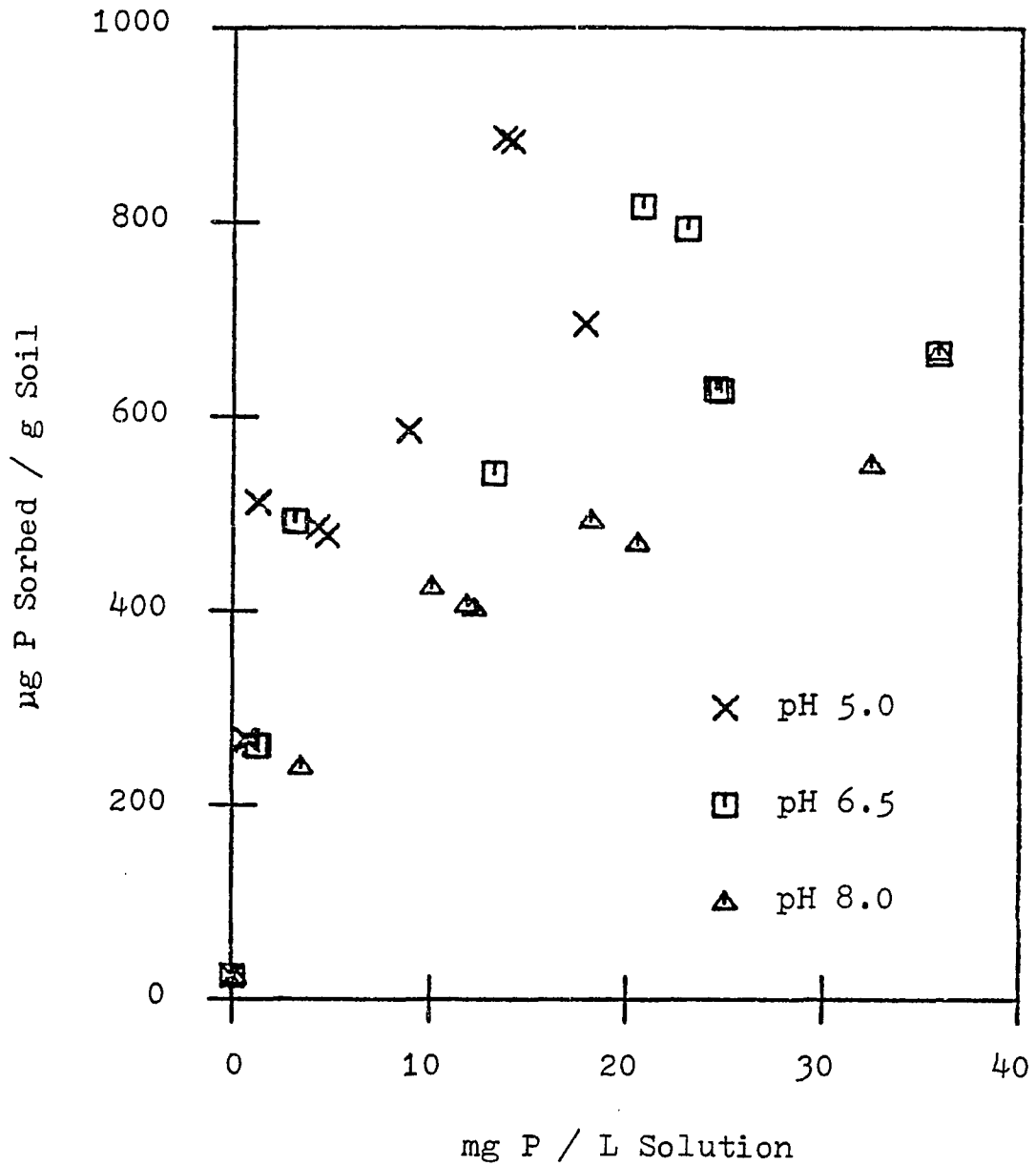


Figure 2a. Phosphate Adsorption Isotherm for Charlton Soil, 24 Hour Equilibration.

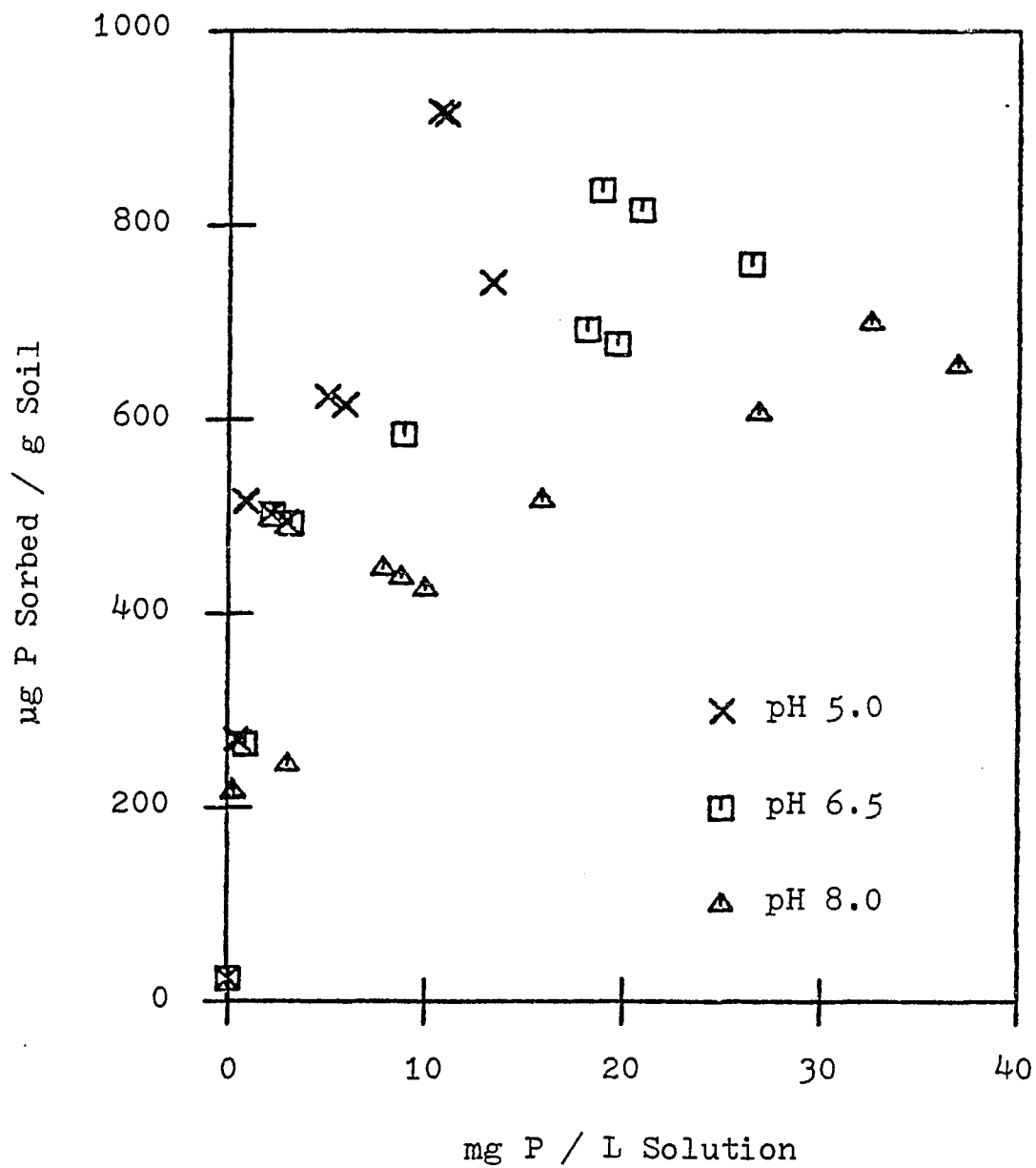


Figure 2b. Phosphate Adsorption Isotherm for Charlton Soil, 48 Hour Equilibration.

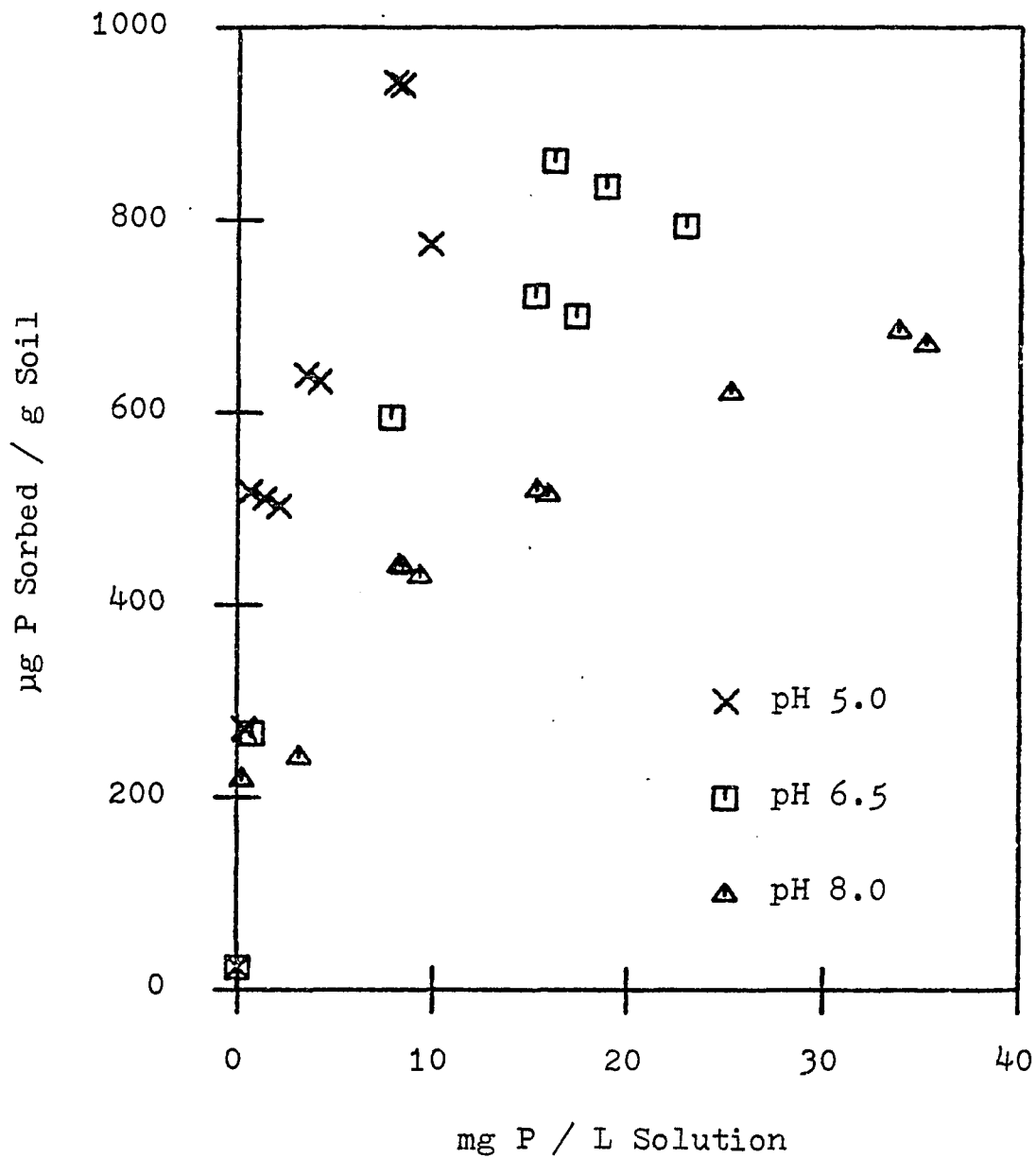


Figure 2c. Phosphate Adsorption Isotherm for Charlton Soil, 72 Hour Equilibration.

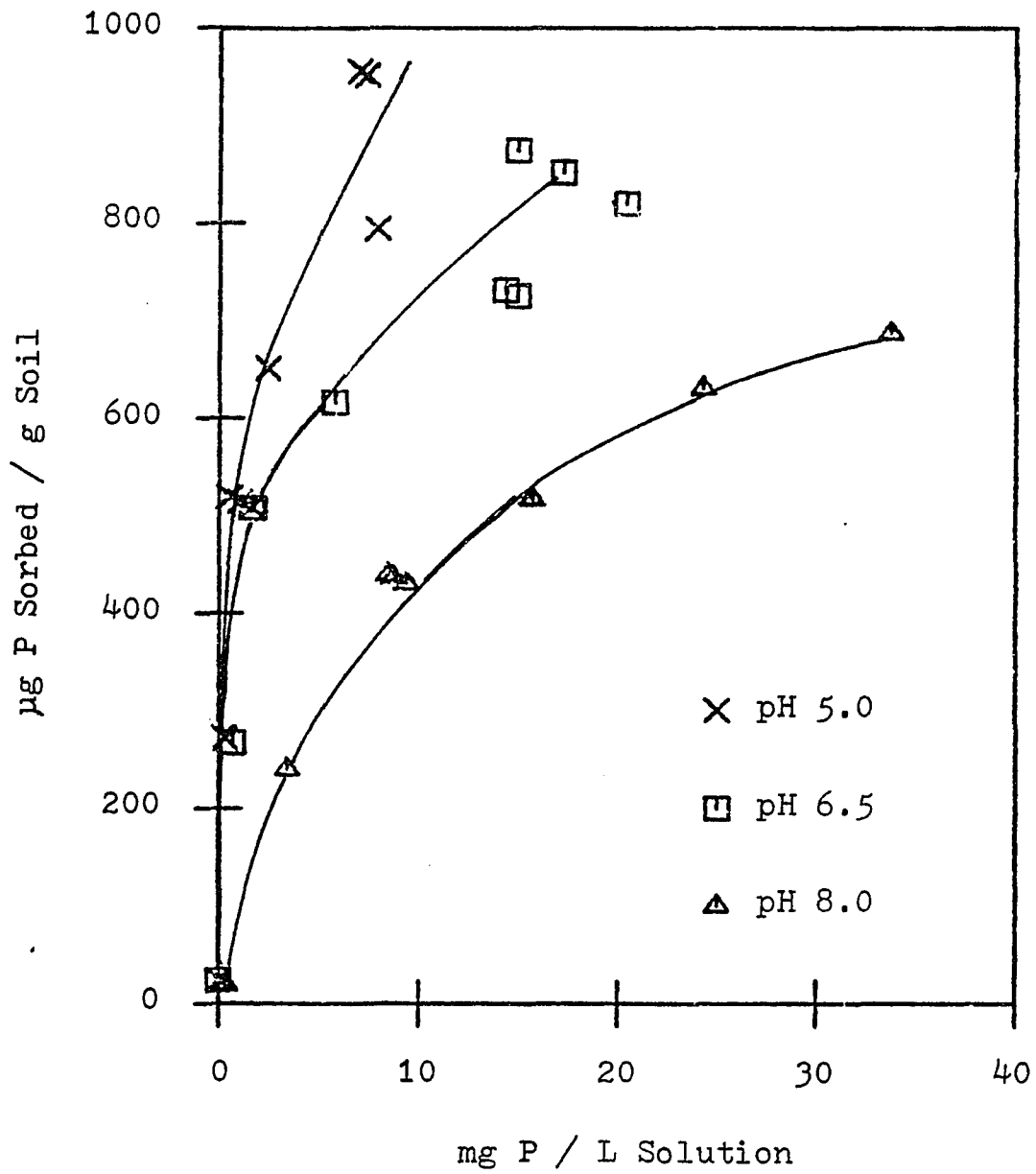


Figure 2d. Phosphate Adsorption Isotherm for Charlton Soil, 96 Hour Equilibration.

Increased solubility of iron and aluminum phosphate compounds at alkaline pH will also contribute to a lowering of the sorption capacity with an increase in pH. The relatively high iron and aluminum content of the Charlton soil indicates that these compounds play an important role in phosphate sorption. Thus, a decrease in phosphate sorption capacity may be expected in alkaline solutions.

Charlton Soil Exchange Studies

The degree to which isotopically labelled phosphate will be removed from solution in a suspension at equilibrium indicates the amount of exchangeable phosphate present in the soil. Since exchange of phosphate between the soil and solution involves a dynamic equilibrium, phosphate will continue to move between sorbed forms and solution forms even at equilibrium. While suspensions in this study are not at true equilibrium after 96 hours of equilibration, the net amount of sorption occurring over the 8 hour equilibration period after addition of radiotracer is very small. An 8 hour equilibration period was used rather than a shorter period as used by Ryden and Syers (1977d) to insure approach to isotopic equilibrium.

The amount of exchangeable phosphate in the soil is calculated as follows.

$$\text{mg P (Ex)/L (Sol'n)} = \text{mg P (Sol'n)} \times \frac{\% \text{ P-32 (Soil)}}{\% \text{ P-32 (Sol'n)}}$$

$$\text{ug P(Ex)/g Soil} = 10 \times \text{mg P(Ex)/L sol'n}$$

The results are presented in Figure 3. The complete set of data is presented in appendix C.

A major portion of the sorbed phosphate is bound as a physically sorbed form which is subject to isotope exchange. The proportion of sorbed phosphate that is exchangeable is quite large and constant within experimental error throughout the concentration range of these isotherms. The plotted lines indicate the least squares fit for the combined pH 5.0 and 6.5 data (A) and pH 8.0 data (B). There is no statistical difference between the pH 5.0 and pH 6.5 data, but the difference between the pooled pH 5.0 and 6.5 data and the pH 8.0 data is significant at the 90% confidence level. The statistical calculations are outlined in Appendix C.

Increased amounts of physically sorbed phosphate can account for the observed pH effect. The mechanisms of Ryden et al. (1977a) propose that phosphate is irreversibly bound on a soil by ligand exchange with either protonated or unprotonated hydroxyl sites. At pH 5.0, many surface hydroxyls will be protonated and phosphate should be

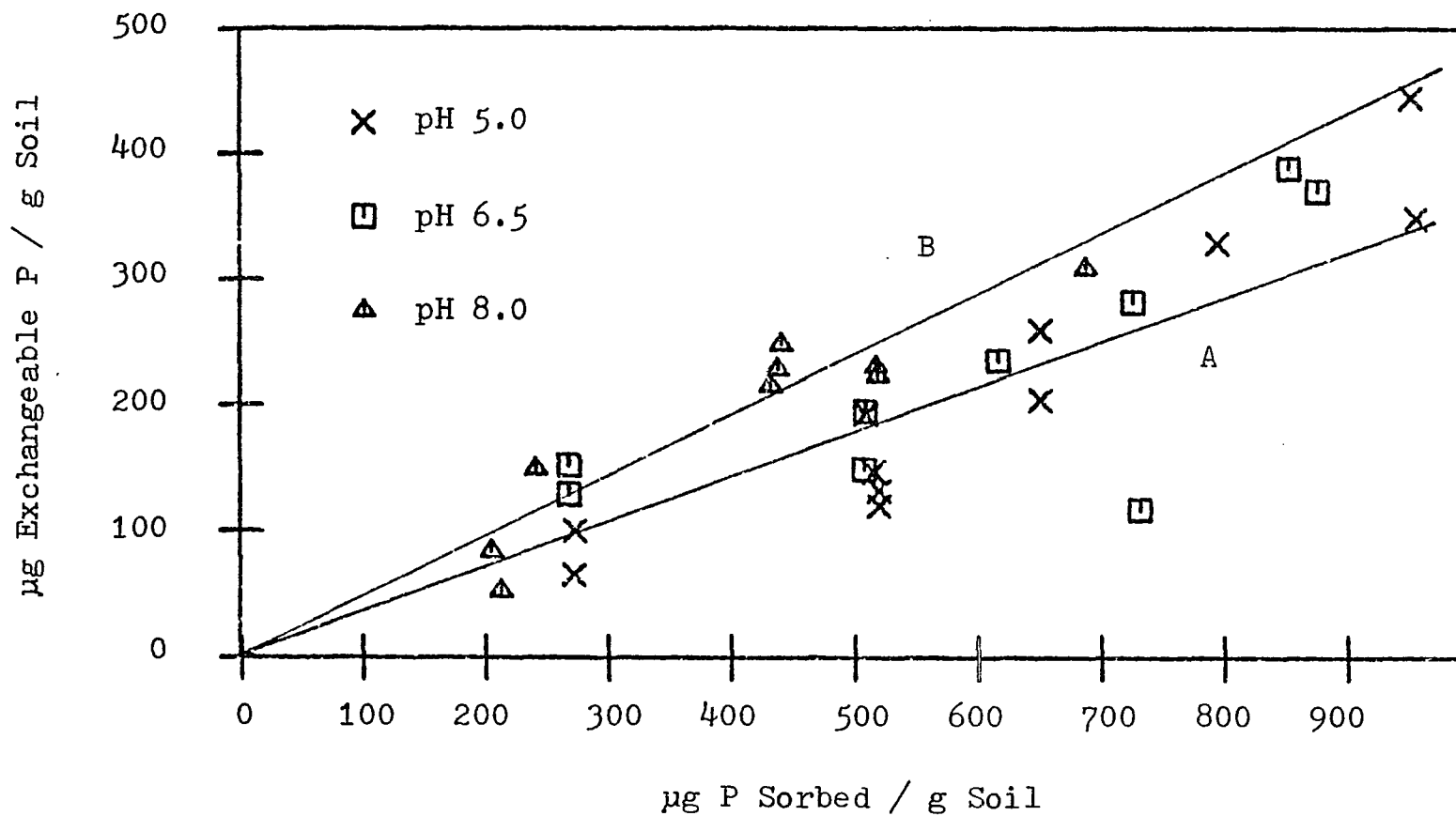


Figure 3. Isotopically Exchangeable Phosphate versus Sorbed Phosphate for Charlton Soil. Least Squares Fit Lines for (A) Pooled pH 5.0 and 6.5 Data, and (B) pH 8.0 Data.

strongly attracted and rapidly converted to chemisorbed P. However, at pH 8.0, the surface charge on the soil is lower and chemisorption would be restricted to non - protonated hydroxyls. As argued above, this decreased surface charge results in generally decreased sorption, but also the lack of protonated ligand exchange sites limits the amount of chemisorption occurring. Thus, a larger proportion of physically sorbed, exchangeable P is expected to be present at alkaline pH in contrast to acidic pH. Suspensions with effluent containing only the natural phosphate level (2.4 mg/L) showed no measureable P in solution at equilibrium and thus no exchangeable P in the soil. In this case it can be assumed that all of the sorbed P was transformed to chemisorbed forms not susceptible to isotope exchange.

Tujunga Soil Sorption Isotherms and Exchange Studies

In contrast, the sorption capacity of Tujunga soil is considerably lower than that of Charlton soil and there is no recognizable pH effect on the sorption behavior. Apparent equilibrium is reached fairly quickly with the Tujunga soil suspensions with little difference seen in the isotherms generated from the 24 hour and 96 hour equilibration data (Figures 4a and b).

The amount of exchangeable phosphate present in the soil is greater than the amount sorbed at the lowest solution concentrations. Exchangeable phosphate represents

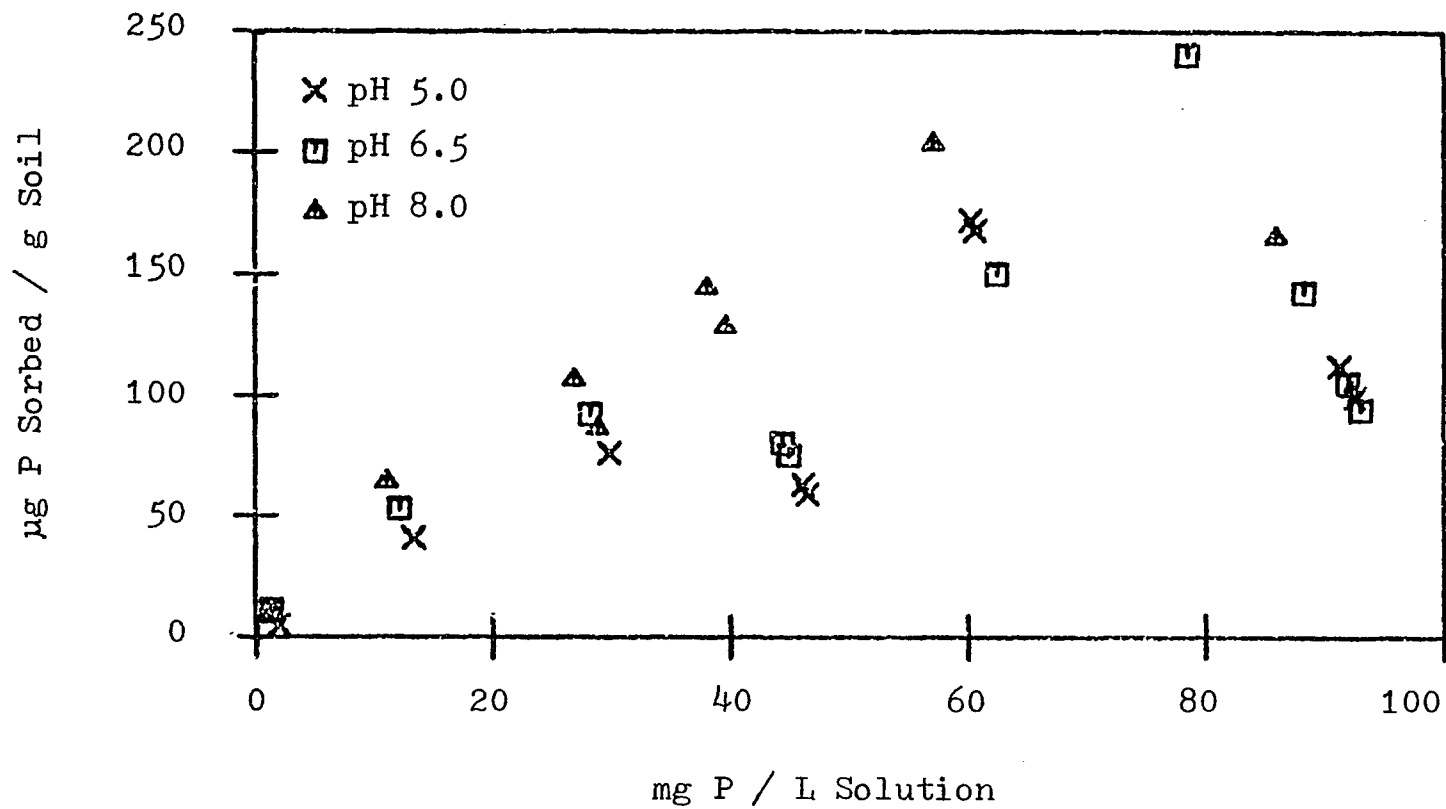


Figure 4a. Phosphate Adsorption Isotherm for Tujunga Soil, 24 Hour Equilibration.

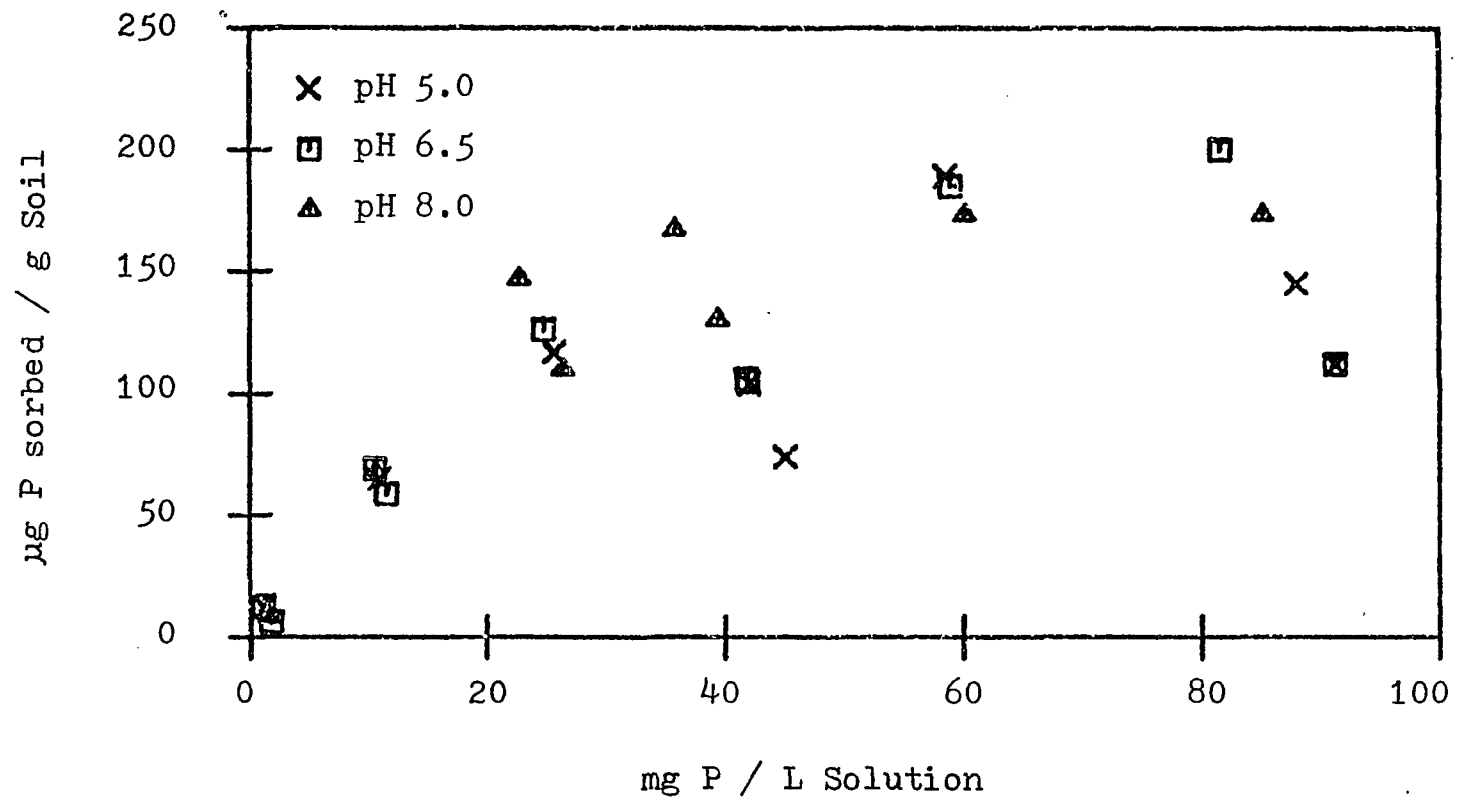


Figure 4b. Phosphate Adsorption Isotherm for Tujunga Soil, 96 Hour Equilibration.

a majority of the sorbed phosphate at all levels of addition (Figure 5). The large amount of scatter in the experimental data is due to increased sampling errors with the coarser Tujunga soil as compared to Charlton soil. Also, the low amounts of P sorbed by this soil make absolute errors of measurement of greater proportional significance than the equivalent errors for Charlton soil. The correlation coefficient for a least squares fit is statistically significant despite the apparent scatter of the data (Appendix C).

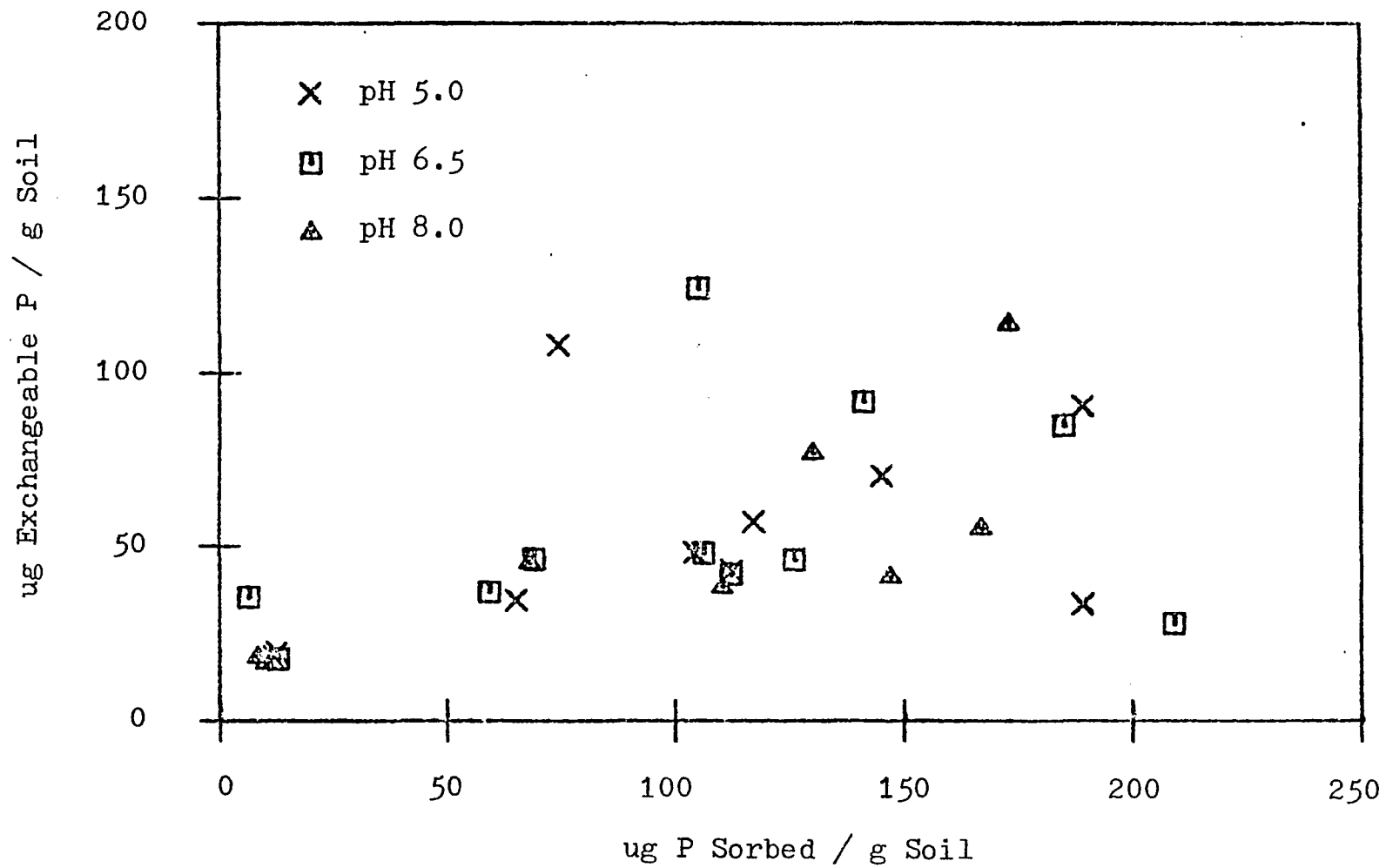


Figure 5. Isotopically Exchangeable Phosphate versus Sorbed Phosphate for Tujunga Soil.

CHAPTER V

KINETIC STUDIES: ADSORPTION AND DESORPTION

Introduction

The rate at which wastewater may be applied to soil while maintaining efficient phosphate removal is important in the design of land treatment systems. Often, the rate of application is based on the permeability of the soil rather than the rate of phosphate removal from the wastewater. If soil permeability is high and the rate of phosphate removal low, solution phosphate may reach very deep soil levels.

Through these kinetic studies of phosphate sorption, contributions of sorption rate differences between the two soils to the problems observed at the Manteca, CA treatment site will be evaluated.

Experimental Procedures

The rates of sorption of phosphate from wastewater at pH's 5.0, 6.5, and 8.0 were measured for both Charlton and Tujunga soils. Air dried ten-gram soil samples were equilibrated with 10 mL of distilled water for 24 hours

before use to insure uniform hydration of the soil. The hydrated soil was mixed with previously described 100 mL portions of homogenized, poisoned wastewater stored in polypropylene storage containers. These containers served as reaction vessels for the sorption studies. The pH was adjusted to the desired value using HCl or NaOH solutions. An Orion Model 701A pH meter fitted with a Corning Cat. No. 476051 rugged duty combination pH electrode was used to monitor the pH of the suspensions. Mixing was accomplished using a Nalgene Floating Stir Bar which maintained vigorous mixing action while avoiding mechanical grinding of the soil by the stir bar.

To enable an unbiased evaluation of the effect of different wastewater pH on the sorption rates for both Charlton and Tujung soils, a completely randomized experiment was designed. For each soil, triplicate sorption experiments were performed for each of the three pH values, using spectrophotometric measurement in one series and P-32 as a radiotracer in a second series. Thus, 36 trials were performed in this scheme (2 soils, at 3 pH's, with 2 analytical methods, all in triplicate).

The sequence in which these trials were performed was decided on the basis of a set of random numbers generated from a simple computer program. Any uncontrolled variations in the trials are randomly distributed throughout the experiment. This allows for a proper statistical evaluation

of the differences among the experimental conditions as well as determination of the general reproducibility of the results.

At periodic intervals, samples of approximately 1.5 mL were removed from the suspensions and filtered through 0.45 um pore size nitrocellulose filters. For spectrophotometric phosphate analysis, a 1.0 mL aliquot of filtrate was immediately diluted to an appropriate concentration and the resulting solution was stored in an acid washed polypropylene bottle at 2°C until analysis was performed. For the P-32 tracer experiments, a 1.0 mL aliquot of the filtrate was transferred to a cupped planchet and dried over low heat. The P-32 radioactivity of the residue was measured using an end - window Geiger - Muller detector connected to a standard scaler and associated electronics. Decay corrections were made for samples measured at different times.

At the conclusion of an adsorption trial, the remaining suspension was filtered through a 0.40 um pore size polycarbonate filter. Polycarbonate filters were chosen for this use due to the difficulties encountered in removing soil samples from nitrocellulose filters. The retained material, which included both wastewater and soil particles, was washed twice with 10 mL portions of 70% methanol - water to remove interstitial solution without displacing bound phosphate. Each sample was then air dried.

After the recovered material for each adsorption trial was dried for a minimum of 48 hours, the soil was resuspended in either 100 mL of unused wastewater or 0.005 M NaCl solution. The sodium chloride solution modeled the ionic strength of the wastewater but contained no phosphate.

Each resulting suspension was adjusted to the same pH as used in the adsorption trial for the soil sample involved. Suspensions were stirred and samples were removed periodically and analyzed as in the adsorption trials. At the conclusion of the desorption experiment, the remaining soil was again filtered and washed with 70% methanol and allowed to air dry.

Results and Discussion

Phosphate Adsorption Trials

Since all adsorption trials were performed in triplicate, each plotted point is a mean of three values. An estimate of the precision of any point was computed as the pooled standard deviation of all trials for each soil and method of analysis. For the P-32 trials, the Charlton soil had an absolute pooled standard deviation of a single datum of 1.79%. Therefore, the standard deviation of a mean of 3 values would be $1.79/\sqrt{3} = 1.03\%$. The corresponding values for the Tujungsa soil are 5.96% and 3.44%. The

primary reason for the greater imprecision for the Tujunga soil is the large fraction of coarse particles, which causes a greater error in sampling.

For the spectrophotometric trials, the imprecision is somewhat greater due to the more extensive sample preparation involved. The Charlton soil pooled standard deviations of single points and means were 3.58% and 2.07% while the corresponding values for the Tujunga soil were 8.31% and 4.80%. The number of degrees of freedom in the calculations for the Charlton soil were only 14 because often the detection capability of the spectrophotometric technique was exceeded for these samples. Thus, many of the samples simply indicated that more than 98.5% of the phosphate was adsorbed.

It is imperative to note the very different behavior indicated by the P-32 and the bulk of the solution phosphate as determined spectrophotometrically. This dramatically illustrates possible errors inherent in using only one of these methods to evaluate the behavior of sorbed phosphate. The radiotracer reflects the behavior of the phosphate initially present in the wastewater. Spectrophotometric monitoring of the solution phosphate shows the net changes of phosphate concentration in solution, including possible release of native phosphate from the soil. Thus, information obtained by using both methods of analysis is complementary.

Phosphate Adsorption by Charlton Soil

Adsorption behavior for the Charlton soil is presented in Figures 6 and 7. Greater than 90% of the phosphate was adsorbed within 30 minutes of mixing the wastewater with the soil in all cases.

The rates of sorption observed were dependent on the vigor of mixing of the suspensions. In preliminary sorption experiments, the suspensions were agitated by bubbling air through the suspensions from an aerator tube located at the bottom of the reaction container. Generally lower amounts of phosphate were removed from the solution using this air agitation compared to mixing with the Nalgene floating stir bar. Reproducibility of the measurements was also much poorer using air agitation.

Barrow and Shaw (1979c) found that rates of sorption vary with the vigor of mixing. They examined three vigorous methods of mixing; rotation of the bottles on a roller, end - over - end shaking at 30 cycles per minute, and reciprocating shaking at 240 cycles per minute. They found higher rates of sorption using the reciprocating shaking with soil particles of unstable structure. They suggested that very vigorous agitation physically broke down the soil particles exposing more reactive materials for sorption.

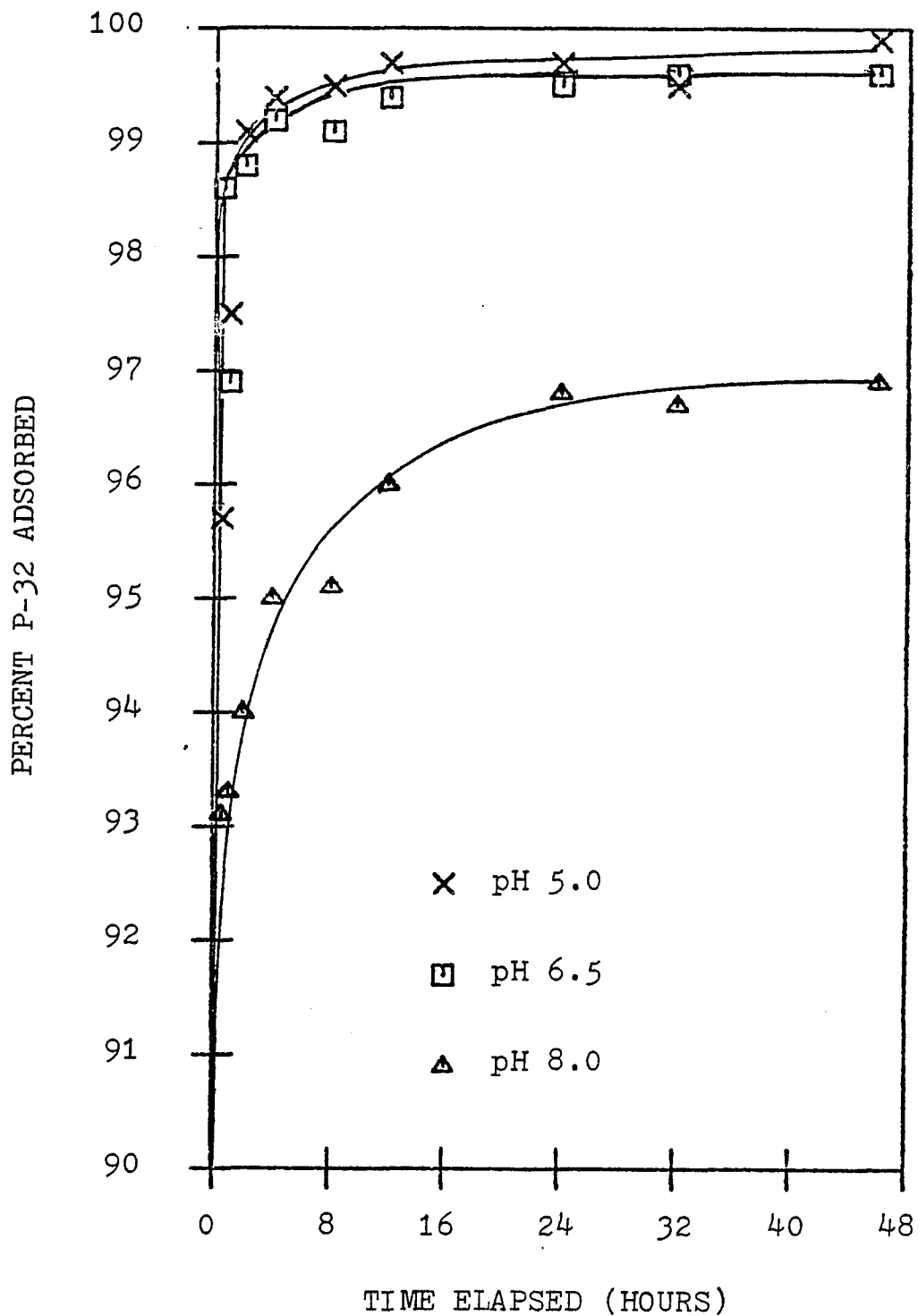


Figure 6. Rate of Adsorption of P-32 by Charlton Soil at pH 5.0, 6.5, and 8.0. (Note Expanded Scale of Abscissa).

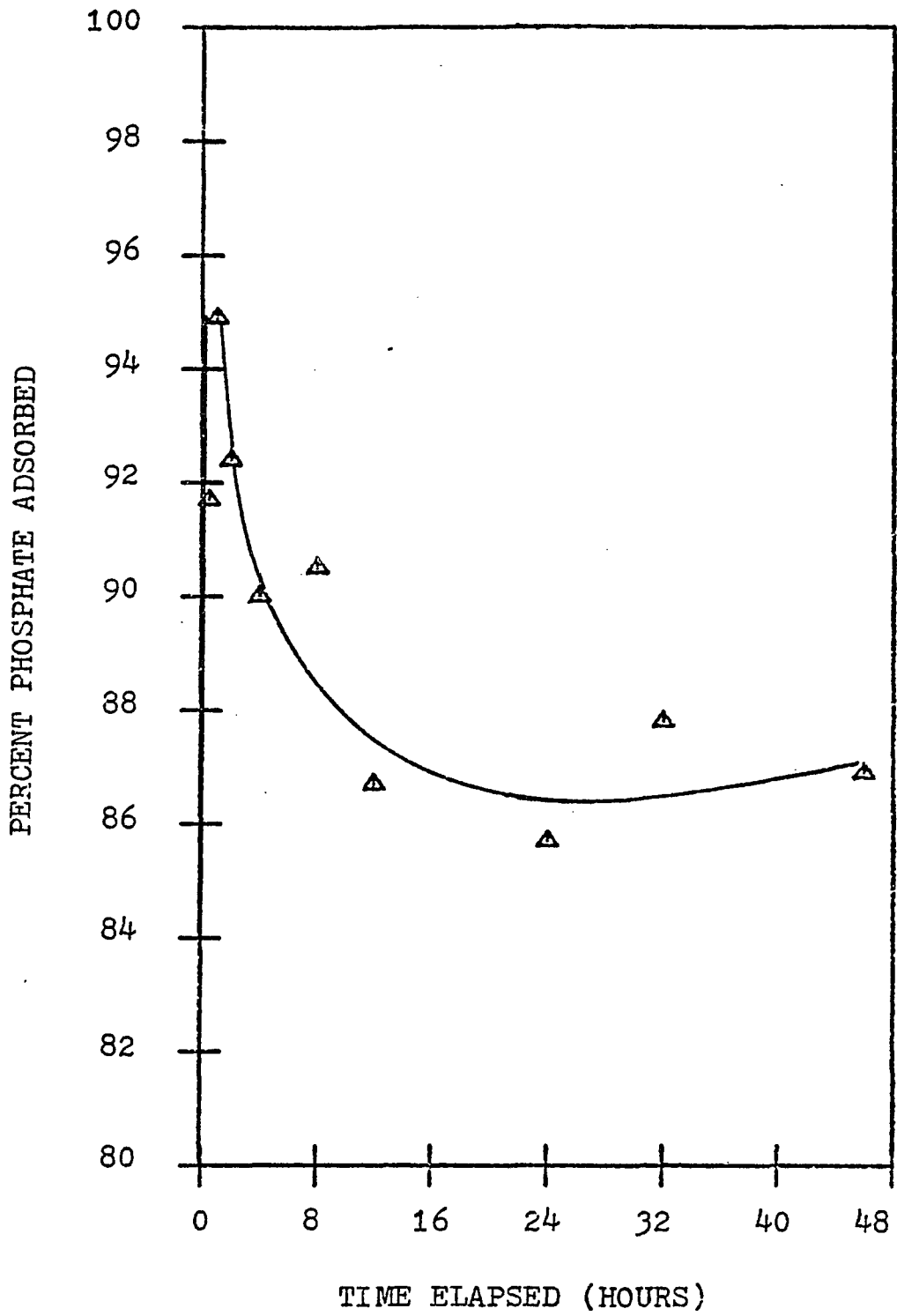


Figure 7. Rate of Adsorption of Non-Radioactive Phosphate by Charlton Soil at pH 8.0. (Note Expanded Scale of Abscissa).

For the experiments in this study, agitation provided by the platform shaker in the equilibrium isotherm studies and the mixing used in the kinetic studies yielded comparable conditions. The isotherm studies carried out with wastewater containing phosphate at the natural level produced results comparable to the kinetic data obtained in similar suspensions. The lower rates of sorption observed with air agitation are quite likely due to less efficient suspension of all the soil particles resulting in reduced mass transfer efficiency.

The P-32 phosphate adsorption (Figure 6) shows almost complete adsorption for the suspensions at pH 5.0 and 6.5, but a significantly lower rate of adsorption at pH 8.0. Likewise for the spectrophotometrically monitored trials (Figure 7), there is no detectable phosphate (<0.04 mg/L) in solution after 30 minutes of equilibration at the two lower pH values. However, the pH 8.0 suspension exhibits a pattern of rapid adsorption followed by a slower release.

Other differences in the pH 8.0 trials were noted. Filtrates of the suspensions acquired a distinct brownish color after 12 hours of equilibration. Also, suspensions became difficult to filter after that period of time. These characteristics were not observed in the suspensions at lower pH. The release of hydrous iron oxides and organic material from the soil would account for both the color development in the filtrate and the filtering difficulties.

Reduced P sorption at pH 8.0 can be rationalized on the basis of the elegant mechanistic proposals of Ryden et al. (1977a). Very low concentrations of P are available for sorption from the wastewater alone, corresponding to 24 ug/g soil. Furthermore, the concentrations of P remaining in solution after 30 minutes are always below 0.3 mg/L and for pH 5.0 and 6.5, they are below 0.04 mg/L. According to Ryden et al. (1977a), at equilibrium we would expect all of this phosphate to have been bound by ligand exchange with either protonated or unprotonated hydroxyl groups. However, our kinetic studies are for times ranging from 30 minutes to 48 hours and, therefore, represent non-equilibrium conditions. According to the proposed mechanism of Ryden, P is initially more physically sorbed followed by a slow transformation to chemisorbed P. Since the surface charge will play a significant role in more physical adsorption, it will affect the apparent sorption rate. At pH 5.0, many surface hydroxyls will be protonated and phosphate would be strongly attracted and rapidly converted to chemisorbed P. Although we did not measure the point of zero charge, the absence of any detectable difference in sorption rates at pH 5.0 and 6.5 suggests that the surface is still highly attractive to the phosphate at the latter pH. However, at pH 8.0, the surface charge on the soil is quite different and the sites available for chemisorption would be restricted to non - protonated hydroxyls. Hence, the lower sorption rate observed is not unreasonable.

Another factor contributing to this pH effect is the increased solubility of iron and aluminum phosphate compounds in alkaline solutions. The relatively high iron and aluminum content of the Charlton soil indicates that these compounds play an important role in phosphate sorption. Thus a decrease in phosphate sorption capacity may be expected in alkaline solutions. The difference in sorption pattern between the spectrophotometric and tracer studies indicates that the phosphate being released is in part native phosphate. This phenomenon is dealt with more extensively in the desorption studies.

Phosphate Desorption by Charlton soil

Desorption studies were designed to evaluate the behavior of sorbed phosphate under two conditions. Re-equilibration of soil in fresh wastewater mimics a repeat application of wastewater after a short dormant period as would occur in many land treatment facilities. Equilibration in 0.005 M NaCl solution provides an evaluation of the stability of the phosphates in the soil, both native and most recently sorbed.

A complete set of results for adsorption, resuspension in wastewater, and resuspension in sodium chloride solution is presented on a single graph for each combination of conditions (Figures 8 through 13). In this way, all the information derived for each set of conditions employed is

presented in a self - consistent manner. For all the figures with the exception of the Tujunga soil at pH 5.0, whenever net adsorption occurs (positive values), percentages are calculated relative to the initial concentration in the filterable fraction of the wastewater (100%). When there is a net desorption (negative values), percentages are calculated relative to the concentration of P removed from the wastewater during the initial adsorption trial.

For the Charlton soil at pH 5.0 and 6.5 using spectrophotometric determinations (Figures 8 and 9), a simple pattern is observed. The "desorption" trials in wastewater produce a net adsorption of P. Reequilibration of the soil with wastewater shows that the capacity to sorb phosphate is, at most, marginally affected by the phosphate sorbed in the initial adsorption trial. Almost identical sorption behavior is observed for the "desorption" in wastewater. Correspondingly, no significant amount of phosphate is found in the sodium chloride solution. Clearly, sorbed P is very tightly bound by the Charlton soil at pH 5.0 and 6.5.

For pH 8.0 (Figure 10), sorption observed for the second volume of wastewater shows a somewhat decreased rate and amount of adsorption, though the large majority of P is again removed from the wastewater.

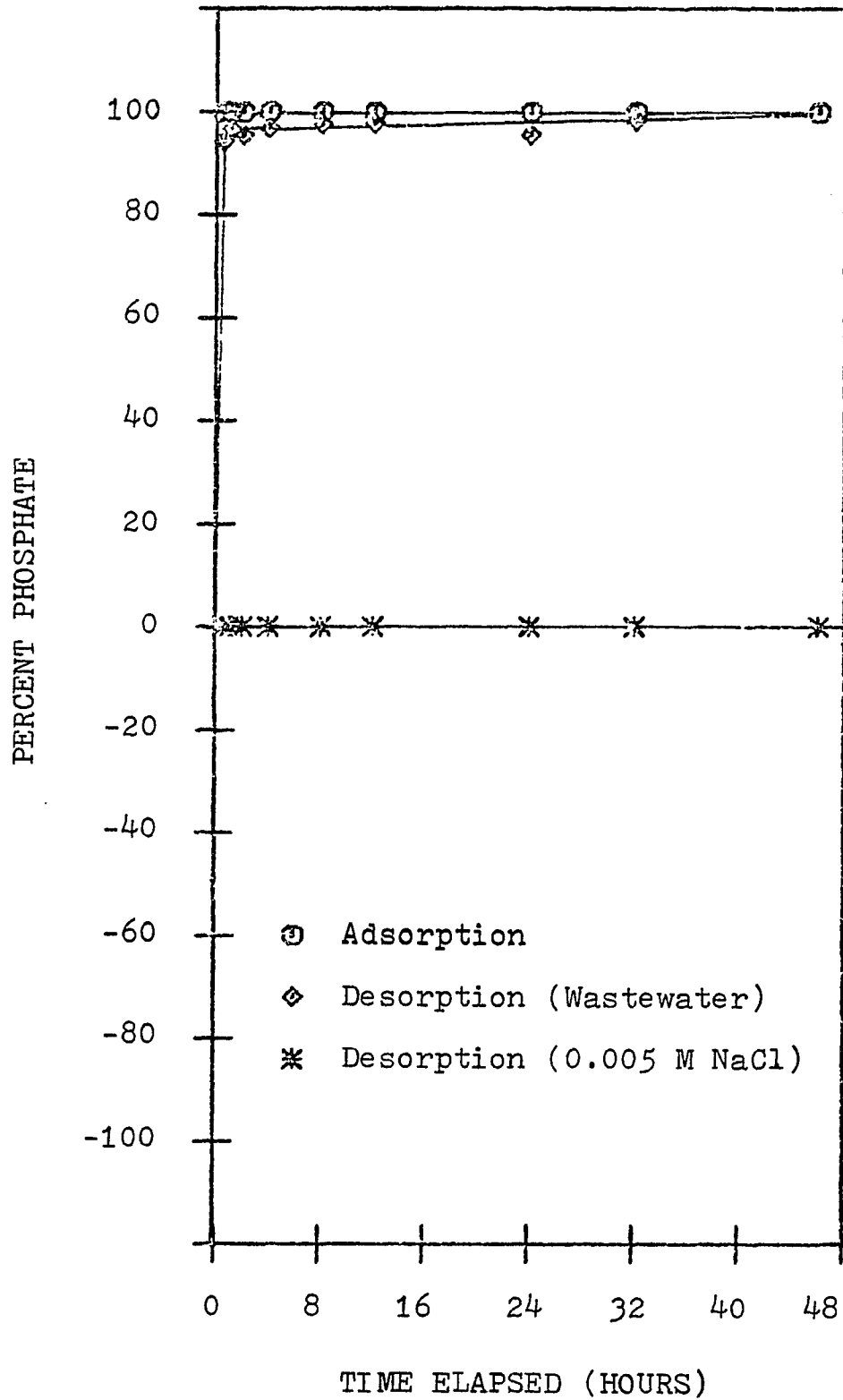


Figure 8. Adsorption - Desorption Behavior of Non-Radioactive Phosphate with Charlton Soil at pH 5.0.

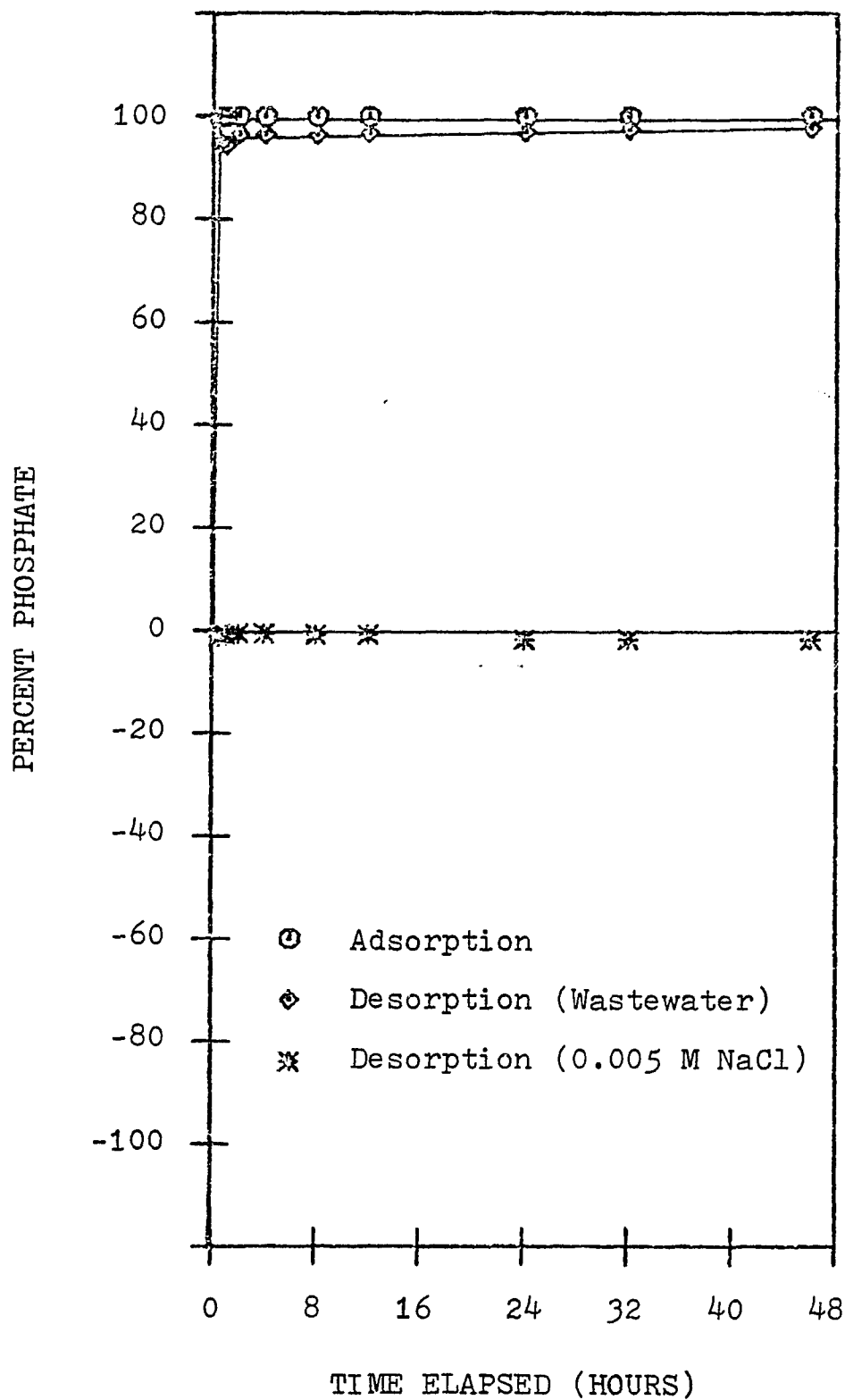


Figure 9. Adsorption - Desorption Behavior of Non-Radioactive Phosphate with Charlton Soil at pH 6.5.

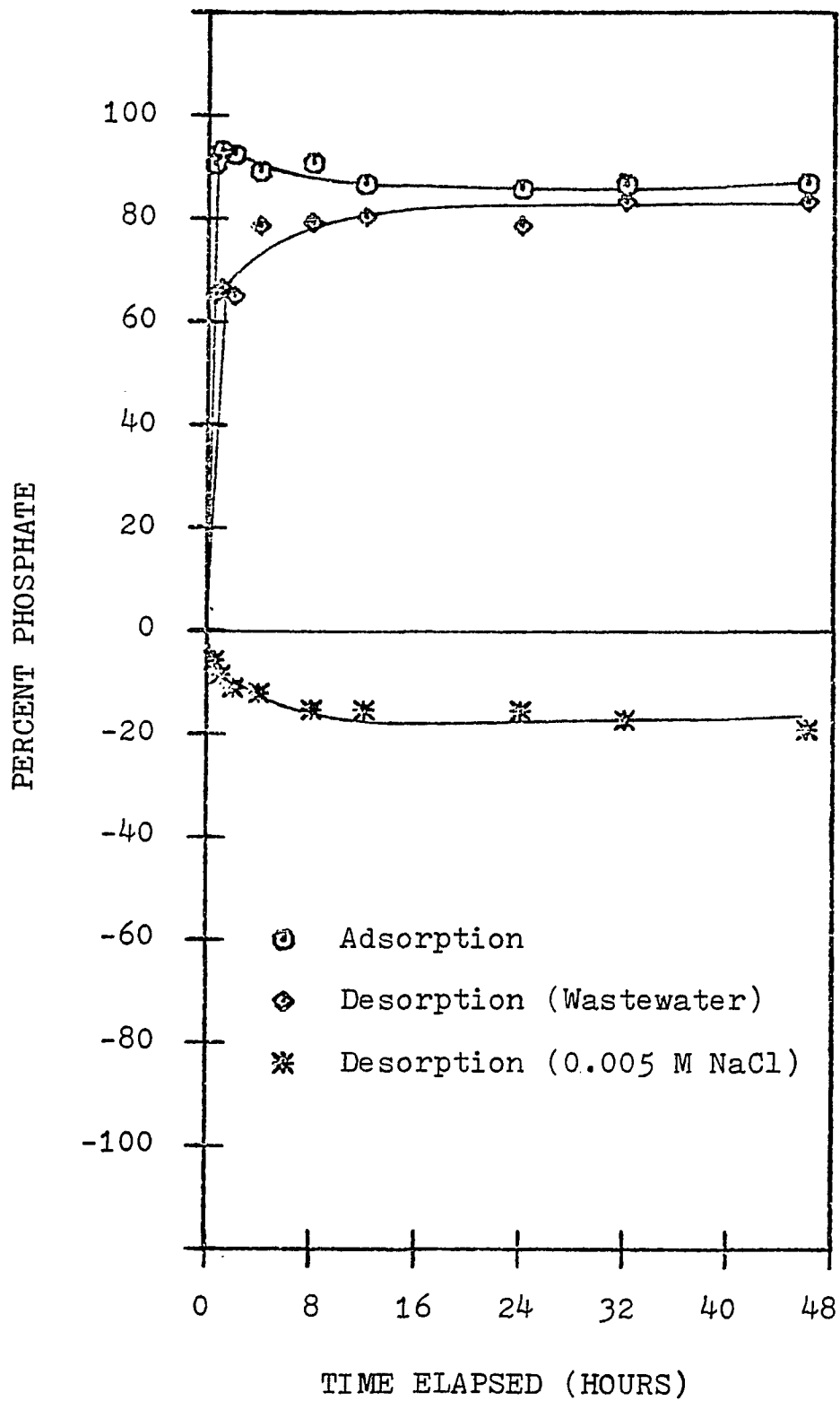


Figure 10. Adsorption - Desorption Behavior of Non-Radioactive Phosphate with Charlton Soil at pH 8.0.

However, in the equilibration with salt solution, a net desorption is seen to the extent of 20% of the phosphate sorbed from the initial adsorption trial. This result is consistent with the explanation of adsorption behavior which considered solubility properties of iron and aluminum compounds and the character of adsorption sites.

For the studies using P-32 (Figures 11-13), the results are complementary to the pattern shown by the spectrophotometric determinations. For pH 5.0 and 6.5, no significant amount of P-32 is released to either the fresh wastewater or the NaCl solution. This indicates that the freshly sorbed phosphate is bound in a stable, insoluble form not subject to isotope exchange. For pH 8.0, however, a very small amount of P-32 is desorbed to the fresh wastewater (~1%), with a significantly greater amount released to the salt solution (~5%). This contrasts to the 20% of phosphate desorbed to the salt solution observed when measured spectrophotometrically. Apparently, 75% of the phosphate desorbed is from native phosphate (possible further dissolution) and 25% is from the freshly sorbed phosphate. Thus, for low amounts of sorbed phosphate, most of the freshly sorbed phosphate in the Charlton soil is either initially bound or is rapidly transformed to very stable forms.

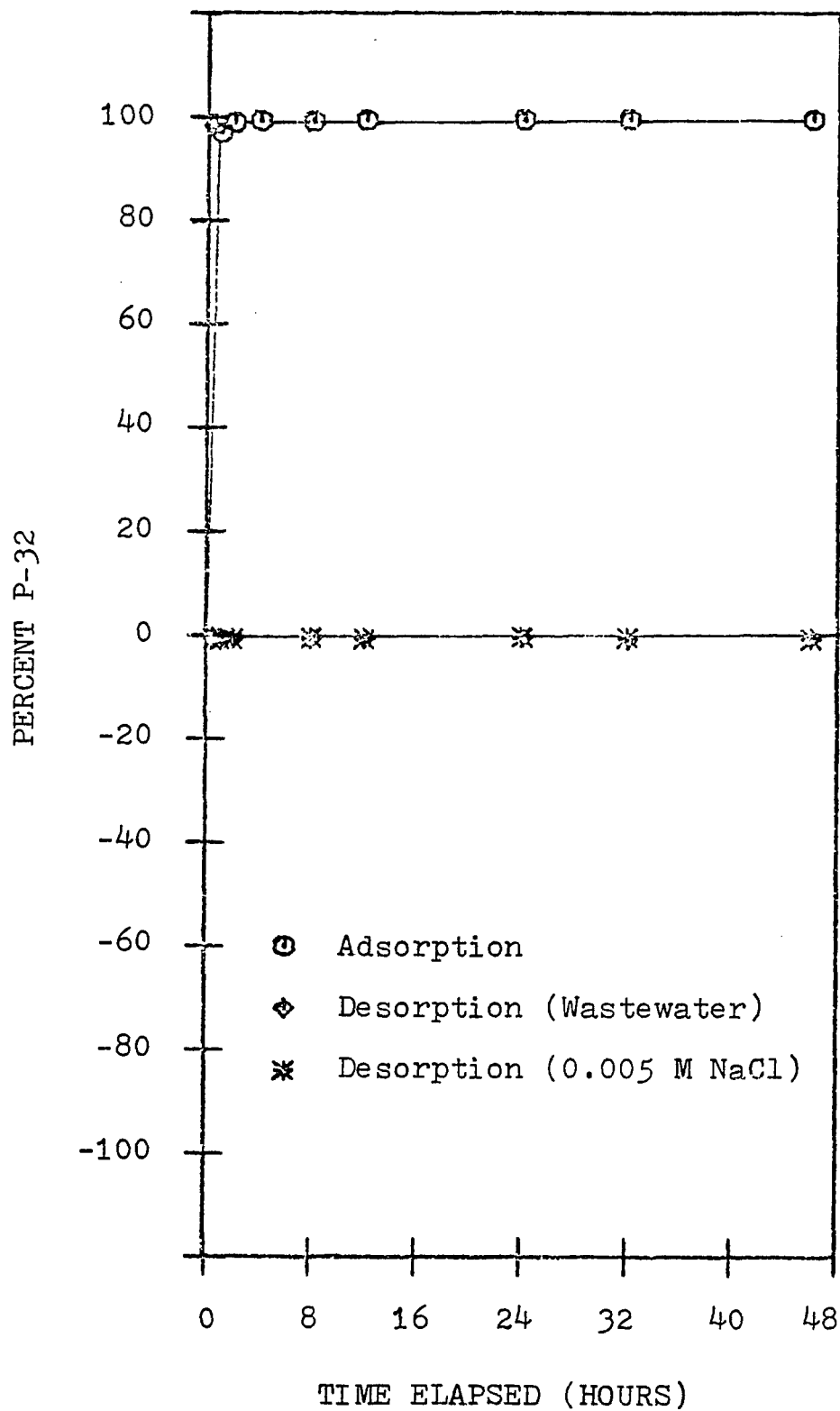


Figure 11. Adsorption - Desorption Behavior of P-32 with Charlton Soil at pH. 5.0.

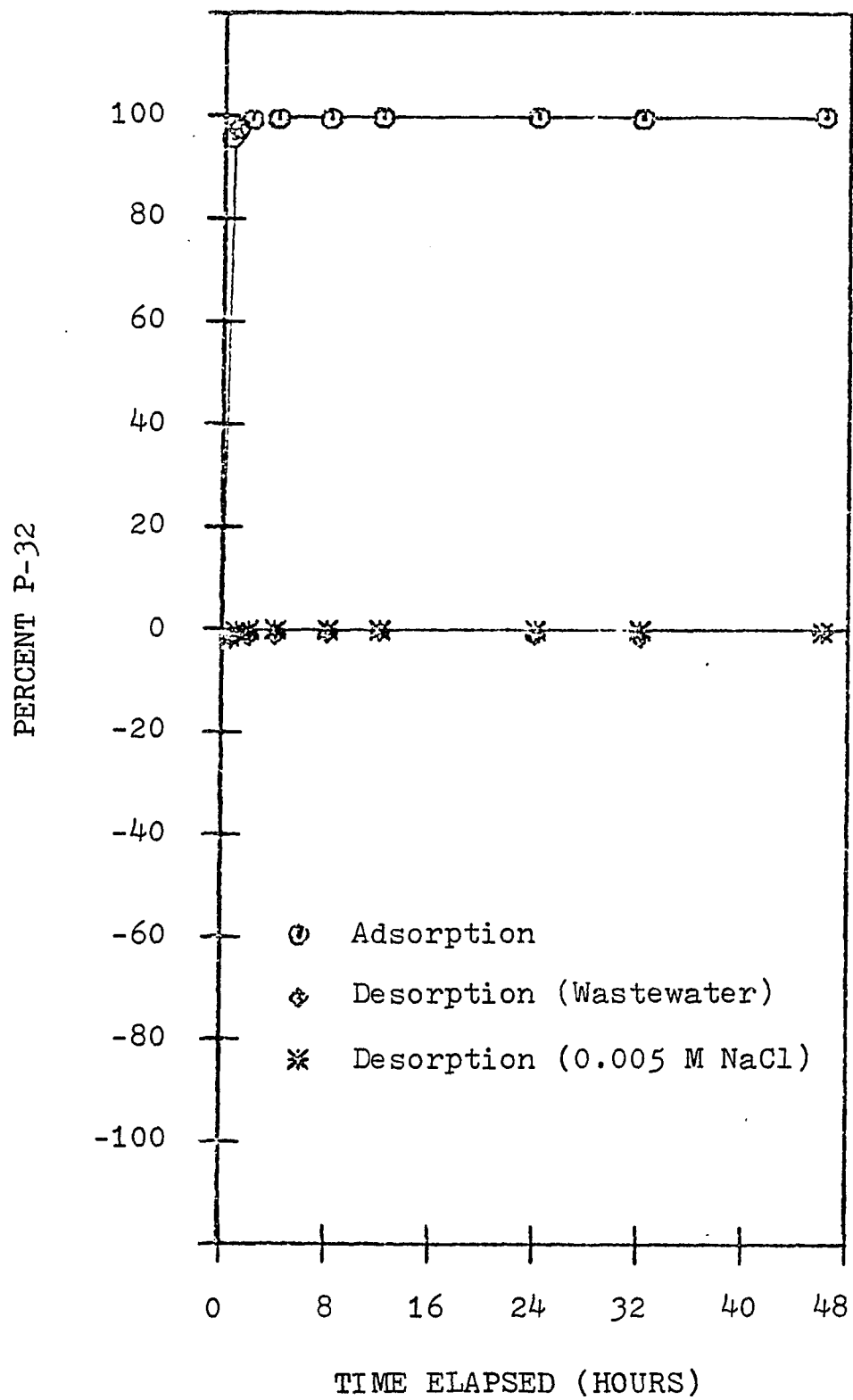


Figure 12. Adsorption - Desorption Behavior of P-32 with Charlton Soil at pH 6.5.

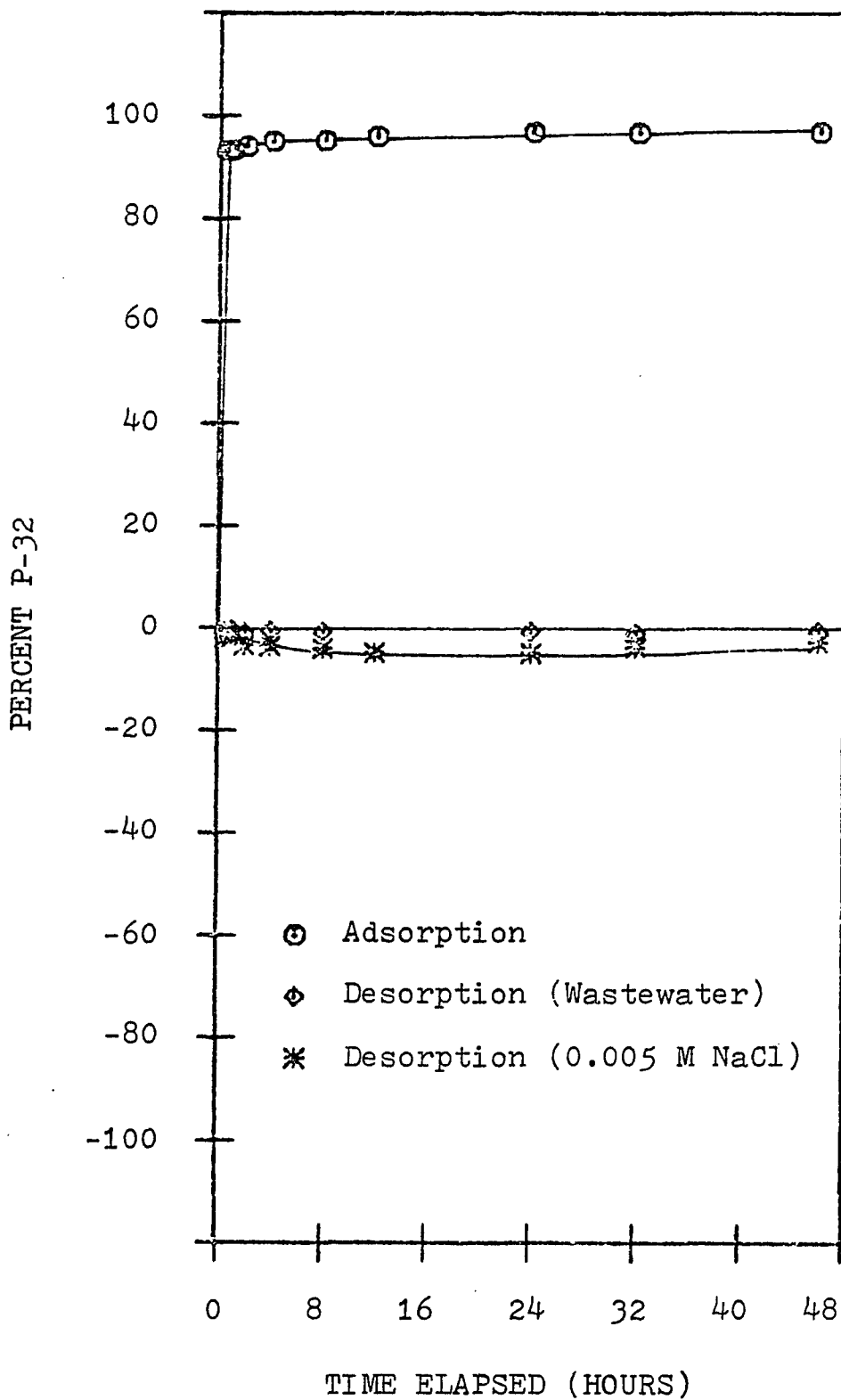


Figure 13. Adsorption - Desorption Behavior of P-32 with Charlton Soil at pH 8.0.

In summary, phosphate adsorption and desorption behavior at pH from 5.0 to 8.0 on the Charlton soil is adequately explained by a combination of the mechanistic proposals of Ryden et al. and solubility properties of phosphate minerals.

Phosphate Adsorption by the Tujunga Soil and Comparison with Charlton Soil

The adsorption behavior for the Tujunga soil is illustrated in Figures 14 and 15. It is immediately obvious that these results present a much more complex and very different picture than the Charlton soil. In what follows, possible explanations of these data will be presented but completely unambiguous statements are not possible.

The P-32 results (Figure 14) show that the rates and amounts of phosphate sorption on Tujunga soil are much lower than for the Charlton soil at all pH's. For example, with the Charlton soil, the minimum percent uptake of P-32 after 30 minutes is 93+% whereas with Tujunga soil, the maximum uptake after 30 minutes is ~48%. After 46 hours, the minimum percent uptake with the Charlton is ~97% where as with Tujunga soil, the uptake is approximately 77% at all pH's. The low sorption capacity of the Tujunga soil is verified by the equilibrium isotherm studies discussed in Chapter 4.

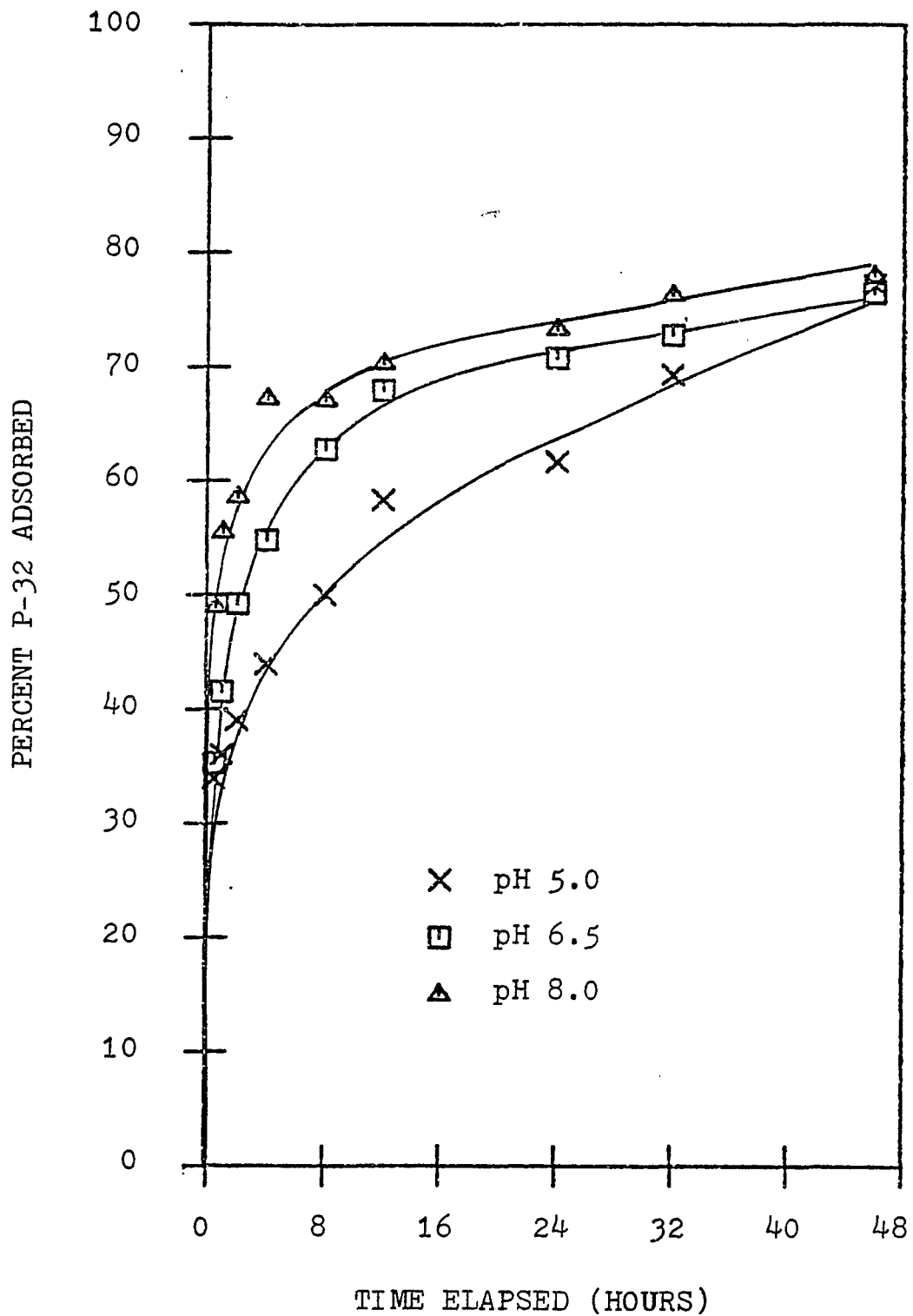


Figure 14. Rate of Adsorption of P-32 by Tujunga Soil at pH 5.0, 6.5, and 8.0.

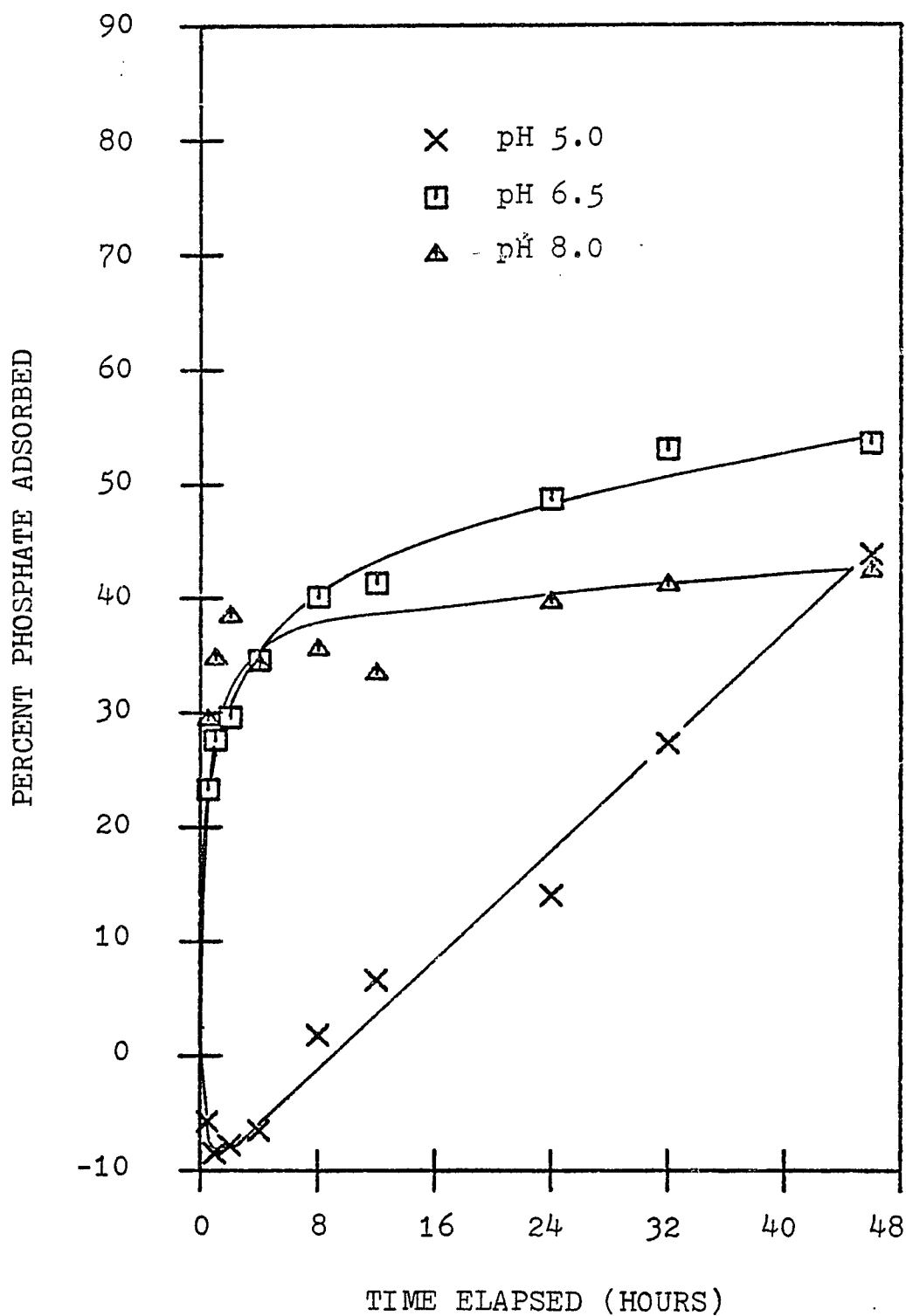


Figure 15. Rate of Adsorption of Non-Radio-Active phosphate with Tujunga soil at pH 5.0, 6.5, and 8.0.

It is also informative to examine the pH effect on the P-32 adsorption with Tujunga soil (Figure 14). At pH 6.5 and 8.0, equilibrium is approached quite rapidly, i.e., the curves have very low slopes after 12 hours. In contrast, at pH 5.0, the initial rate is slow but uptake continues at a significant rate throughout the 46 hour equilibration period. This pH effect is the inverse of that observed for the Charlton soil and suggests that different mechanisms are operating.

Comparison of P-32 results in Figure 14 with spectrophotometric results in Figure 15 reveals a much lower percent P uptake for the latter. The difference is likely due to the combined contributions of isotope exchange and dissolution of native P. Evidence to be discussed in conjunction with desorption experiments will argue that dissolution is the dominant effect at low sorbed P levels. Further comparison between Figures 14 and 15 show that pH effects are similar with both types of measurement. At pH 6.5 and 8.0, equilibrium is rapidly approached, especially at pH 8.0. At pH 5.0, a net desorption of P from the soil is observed for the first two hours, followed by a slow but constant rate of adsorption. After 46 hours, the net adsorption is equal to that for pH 8.0.

It is impossible to give an unequivocal mechanistic explanation of the pH 5.0 behavior. However, one possibility is that there are small amounts of calcium

phosphate compounds which are significantly soluble at pH 5.0. There is other evidence of the presence of soluble phosphate in the Tujunga soil. For example, ammonium chloride extraction (Table 4) indicated 5 $\mu\text{g/g}$ of soluble phosphate. Iskandar and Syers (1980) have reported significant amounts of water soluble P in this soil. Based on a soluble P concentration of 2.40 mg/L in the wastewater, the release of 50 μg of P from 10 g of soil to 100 mL of wastewater would increase the concentration to 2.90 mg/L, or a 20% increase. In Figure 15, this would appear as a 20% desorption (assuming no simultaneous adsorption to compensate). Since the observed increase in concentration was only 8%, this rationalization seems plausible. Incidentally, the P release assumed in the above calculations only amounts to about 1% of the total P of Tujunga soil.

We should also note that the amount of P required for the above calculations could be contributed by the release of weak physically sorbed phosphate. According to sorption isotherms generated by Ryden et al. (1977a, 1977b), when the equilibrium concentration of soluble P is 1 mg/L or greater, the predominant amount of P sorbed by a soil is in this physically sorbed form. Although the experiments in this series do not represent equilibrium conditions, in all cases, there is 1 mg/L or more phosphate remaining in solution after 46 hours of equilibration.

The isotope exchange studies discussed previously support the argument that much of the sorbed P is in a physically sorbed, exchangeable form. The isotope exchange studies showed that there was more exchangeable P present than freshly sorbed P at low loadings of P. Much of the native phosphate is, therefore, in an exchangeable form. If inadequate chemisorption sites are present in the Tujunga soil to immobilize the native phosphate, little added phosphate can be expected to be strongly bound. The absence of a pH effect on the exchangeability of sorbed P also argues for the saturation of chemisorption sites on the Tujunga soil. If most hydroxyl sites have already bound phosphate or other materials, protonation of the sites will be limited and will have little effect on surface charge or chemisorption.

Phosphate Desorption by Tujunga Soil and Comparison with Charlton Soil

The desorption behavior of the Tujunga soil also indicates that more complex equilibria within the soil are involved as compared to the Charlton soil. Consistent with the adsorption experiments for the Tujunga soil, the pH 5.0 desorption trials show behavior substantially different from the other pH values (Figure 16 through 18).

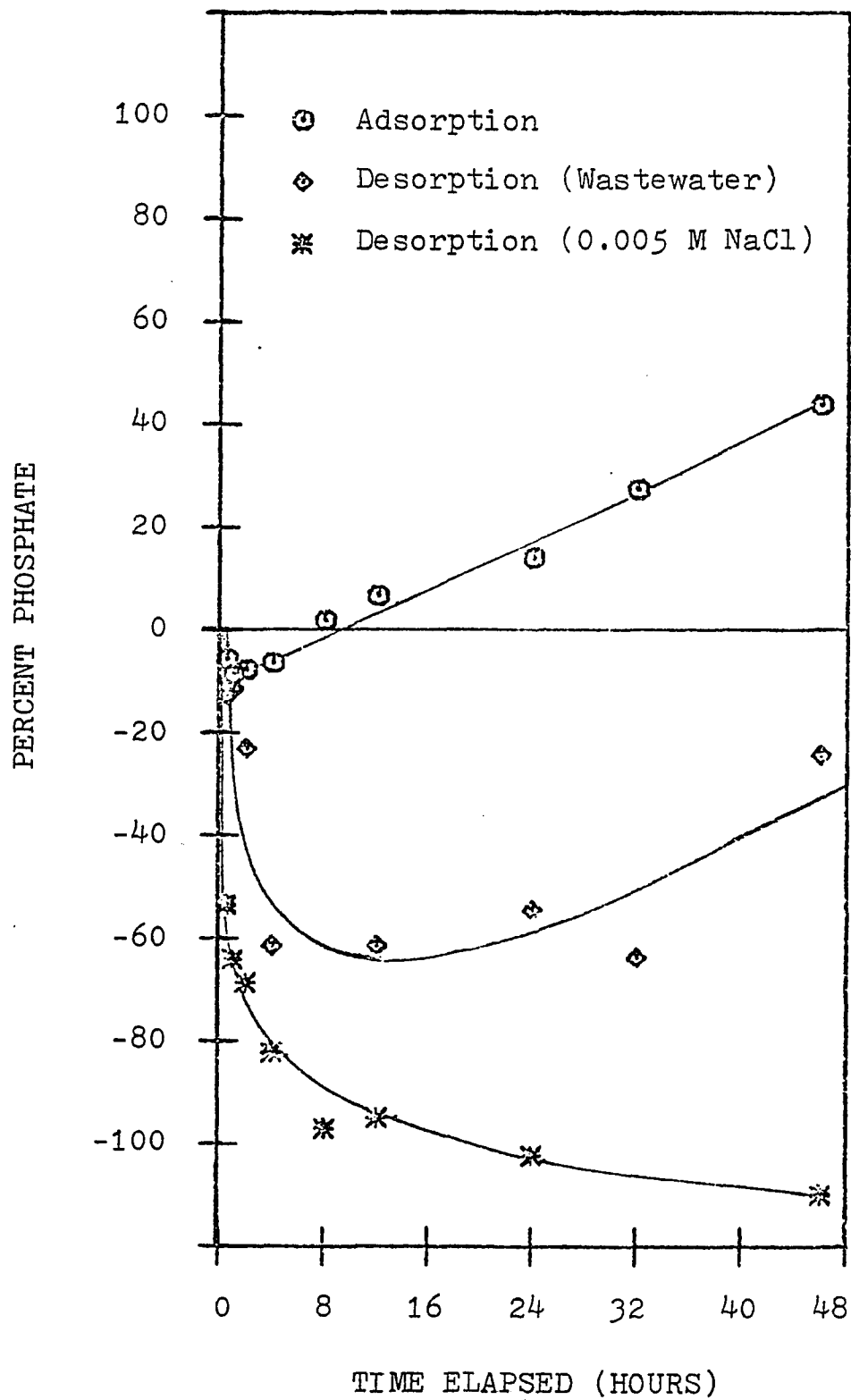


Figure 16. Adsorption - Desorption Behavior of Non-radioactive Phosphate with Tujunga Soil at pH 5.0.

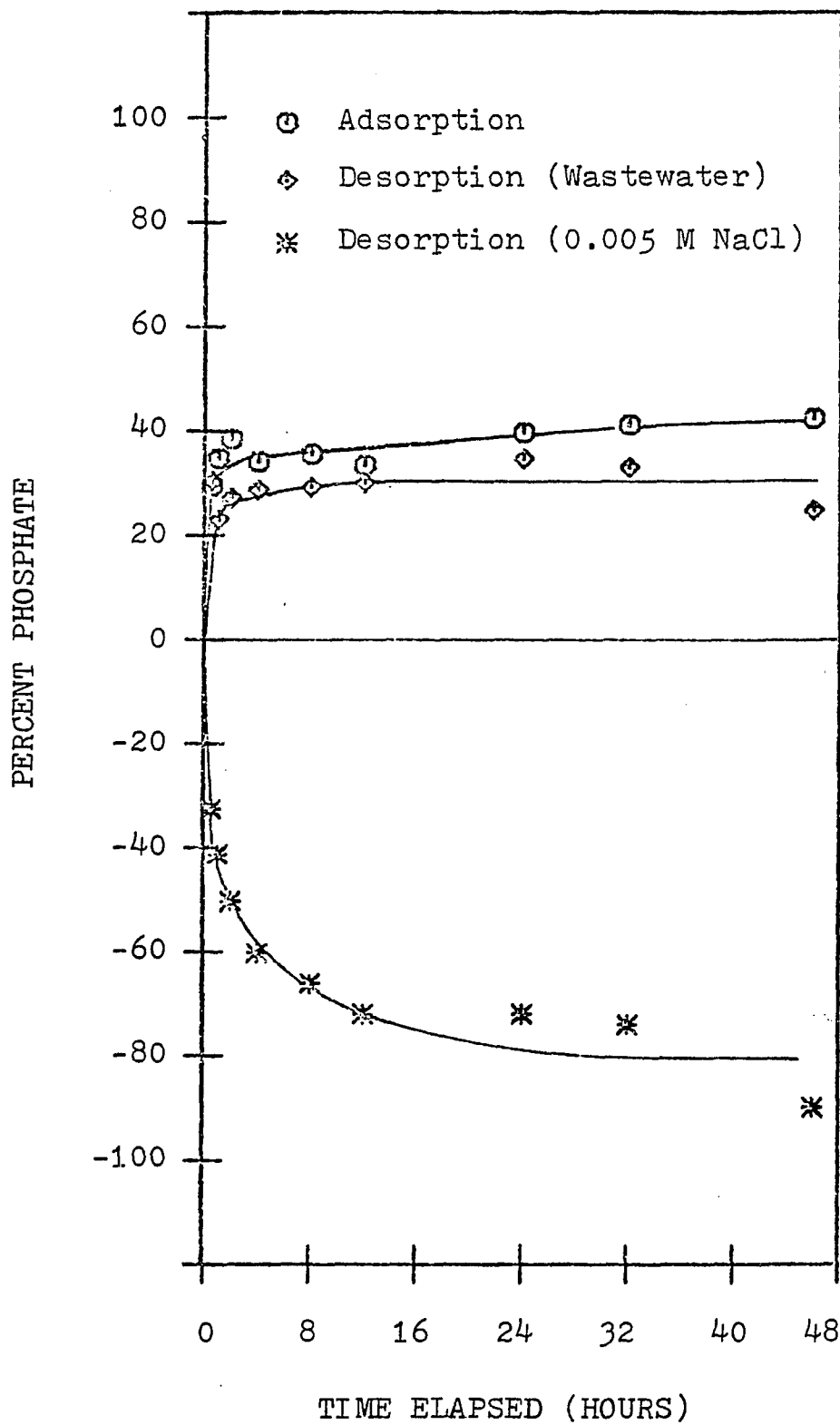


Figure 17. Adsorption - Desorption Behavior of Non-Radioactive Phosphate with Tujunga Soil at pH 6.5.

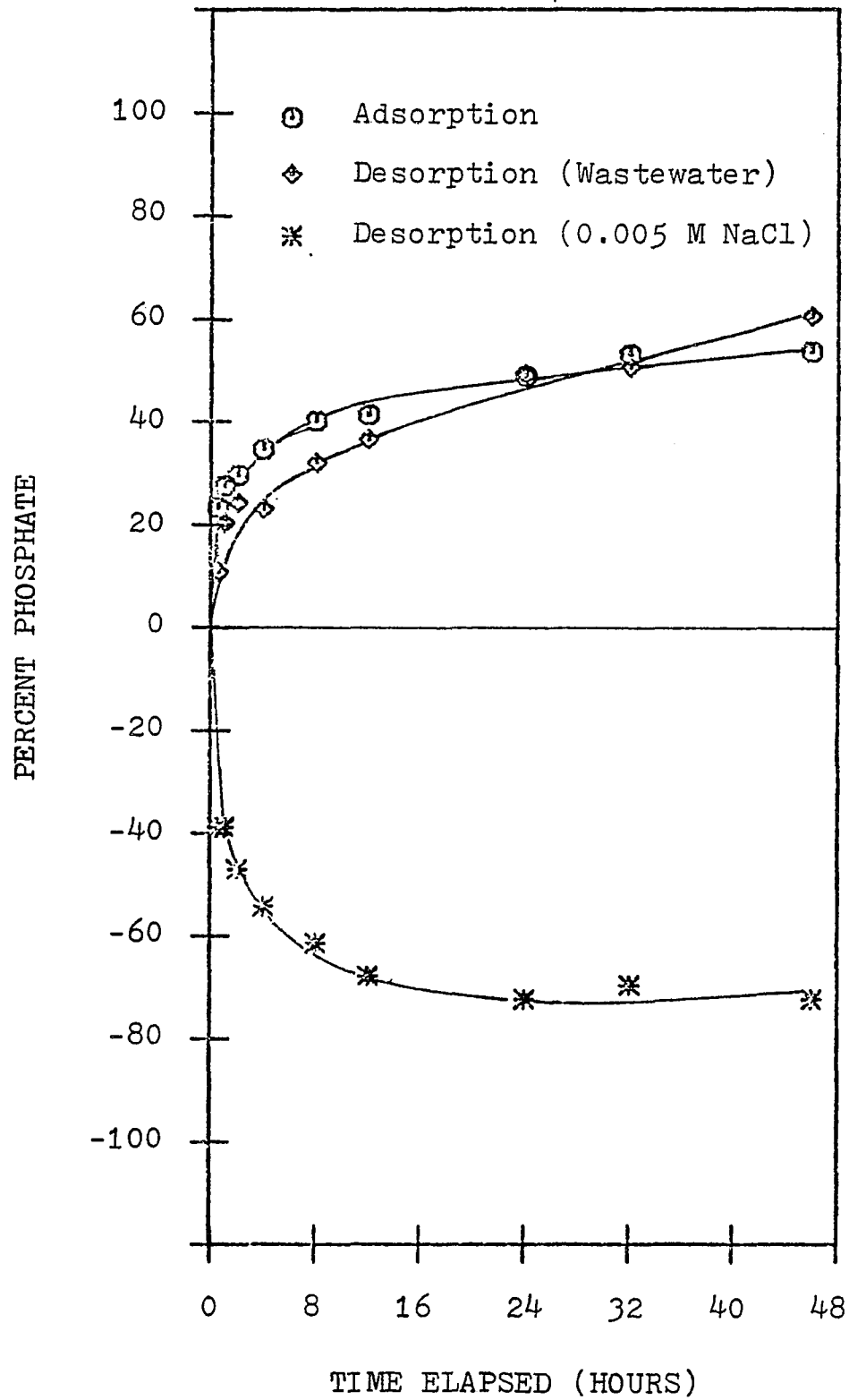


Figure 18. Adsorption - Desorption Behavior of Non-Radioactive Phosphate with Tujunga Soil at pH 8.0.

Spectrophotometric monitoring at pH 6.5 and 8.0 (Figures 17 and 18) show adsorption upon reequilibration with fresh wastewater occurring at an amount almost equal to the initial adsorption trials. Equilibration with the sodium chloride solution results in a large amount of desorption (70% at pH 6.5 and 80% at pH 8.0), clear evidence that most of the sorbed P is readily desorbed in a solution containing no phosphate. Actual solution concentrations of P in the NaCl solutions after 46 hours are 0.7 - 0.8 mg/L, large enough to support the argument that the P is in a physically sorbed form (See previous section). The pH 5.0 desorption results (Fig. 17) show an overall net desorption in both the wastewater and salt solution. In fact, in the salt solution, an amount of phosphate is released greater than 100% of the amount sorbed by the soil in the initial adsorption trials. The pattern of sorption upon reequilibration with wastewater at pH 5.0 parallels the original adsorption except that a greater amount of phosphate is initially released from the soil. Apparently, the form of sorbed phosphate present is very easily solubilized at pH 5.0.

While no pH effect was found in the sorption isotherms for the Tujunga soil, any effects which may be present might be obscured by the approach to phosphate saturation of the soil. Also, since the most obvious effects of pH are in the first two hours of equilibration, the infrequent sampling times used in the isotherm studies may have missed the early

effects. Thus the pH effects on the sorption isotherms may simply be unresolvable given the data obtained.

The radiotracer studies for the Tujunga soil (Figures 19,20,21) show that considerably less P-32 is desorbed than the net amounts of phosphate released as indicated spectrophotometrically. Furthermore, less P-32 is desorbed from the soil into the sodium chloride solution than in the fresh wastewater at pH 5.0 and 6.5 - opposite to all other desorption results. This indicates that the desorption with Tujunga soil involves more than the solubility of the phosphate forms of the soil. Isotope exchange occurs to a large degree. The fact that phosphate present in the wastewater increases the amount of P-32 released indicates that a dynamic equilibrium with rapid exchange is involved in the adsorption/desorption behavior of the Tujunga soil.

The amount of P-32 desorbed to the fresh wastewater increases substantially with a decrease in pH, but the amount of P-32 desorbed in the NaCl solution remained practically constant with pH. Apparently, the degree to which isotope exchange occurs is sharply increased at pH 5.0. No such effect was observed in the isotope exchange studies made in conjunction with the adsorption isotherms, but the noticeable effect may be limited to systems containing relatively low amounts of phosphate. The relative amount of phosphate exchangeable at pH 5.0 may be obscured by the large amounts of phosphate remaining in

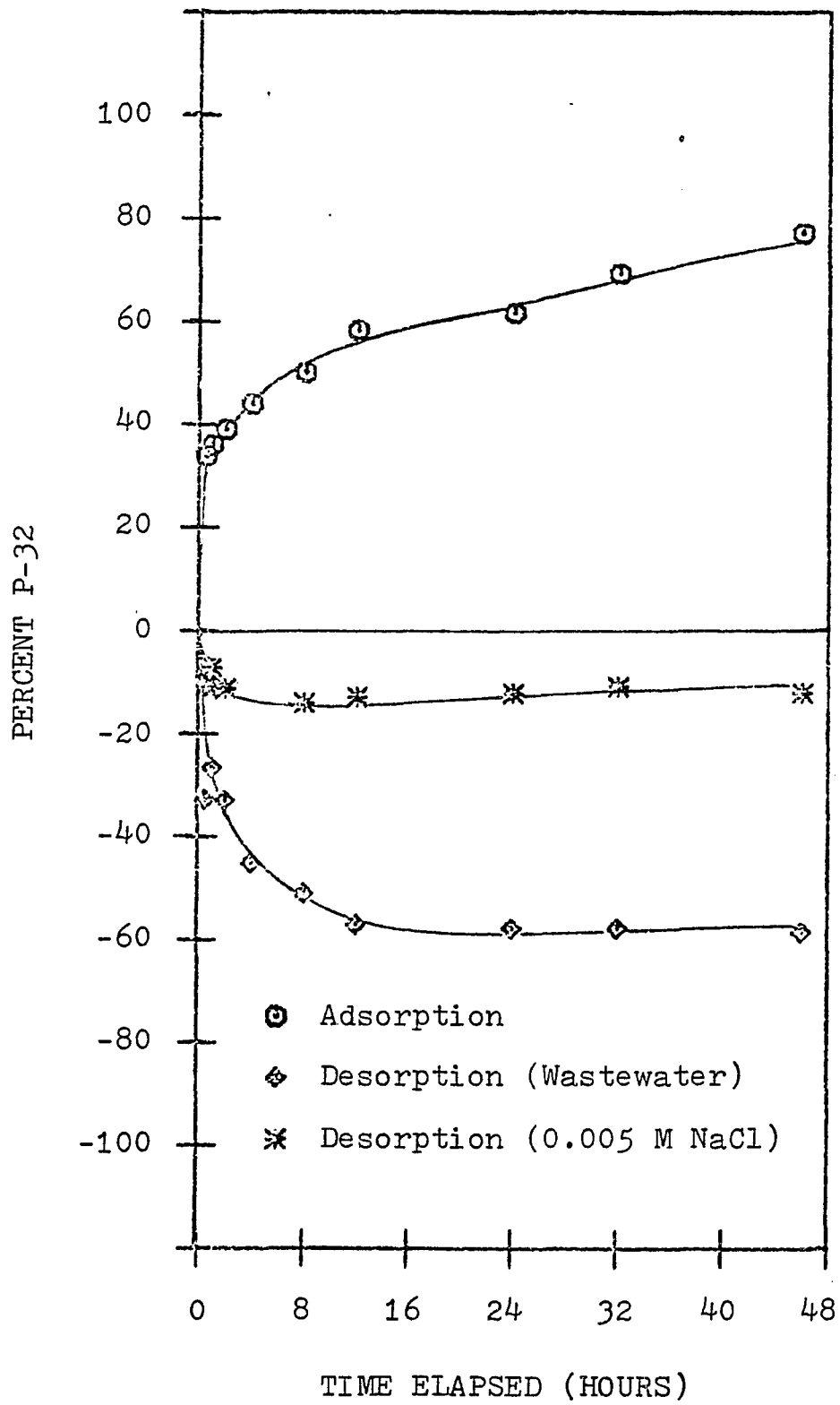


Figure 19. Adsorption - Desorption Behavior of P-32 with Tujunga Soil at pH 5.0.

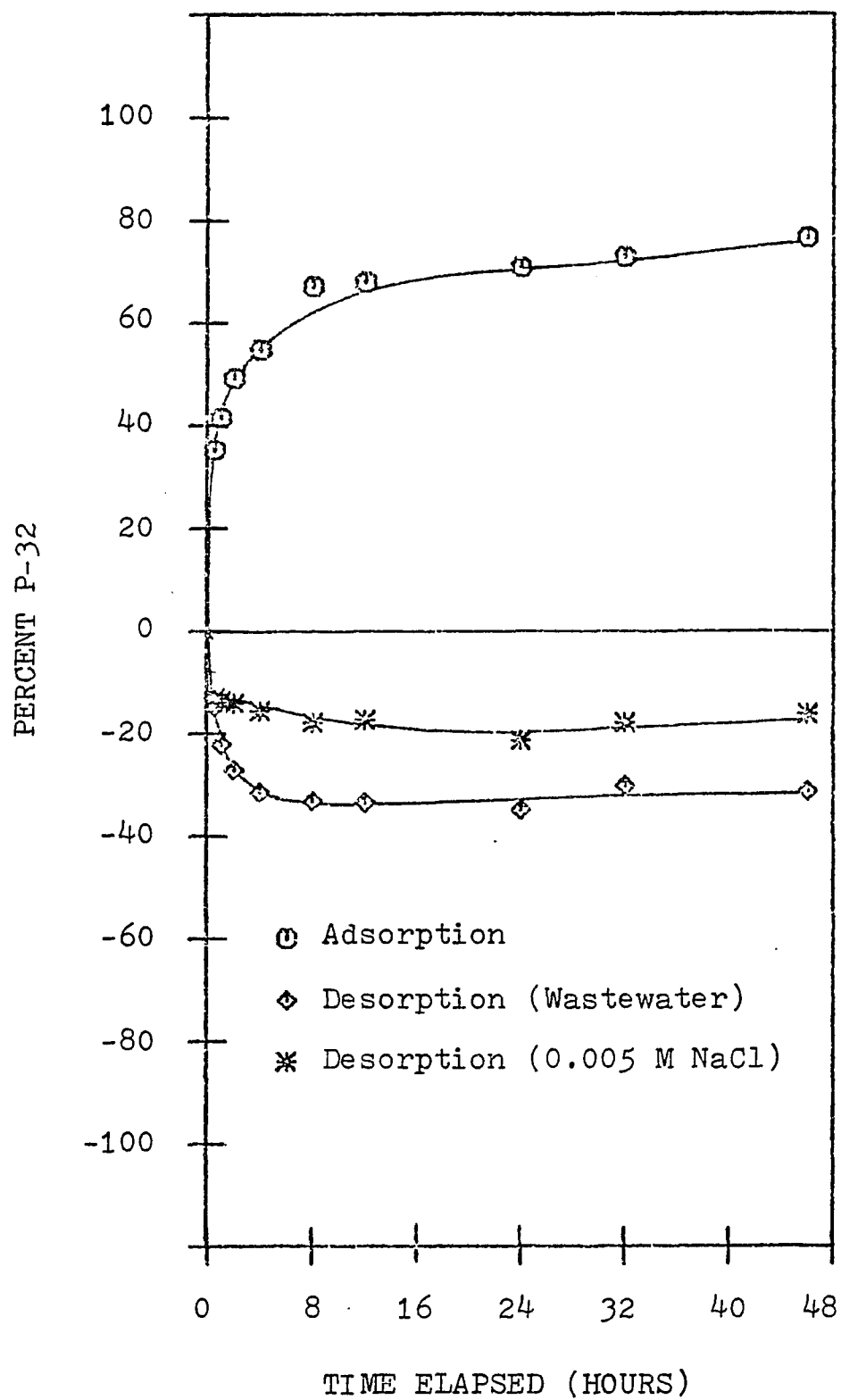


Figure 20. Adsorption - Desorption Behavior of P-32 with Tujunga Soil at pH 6.5.

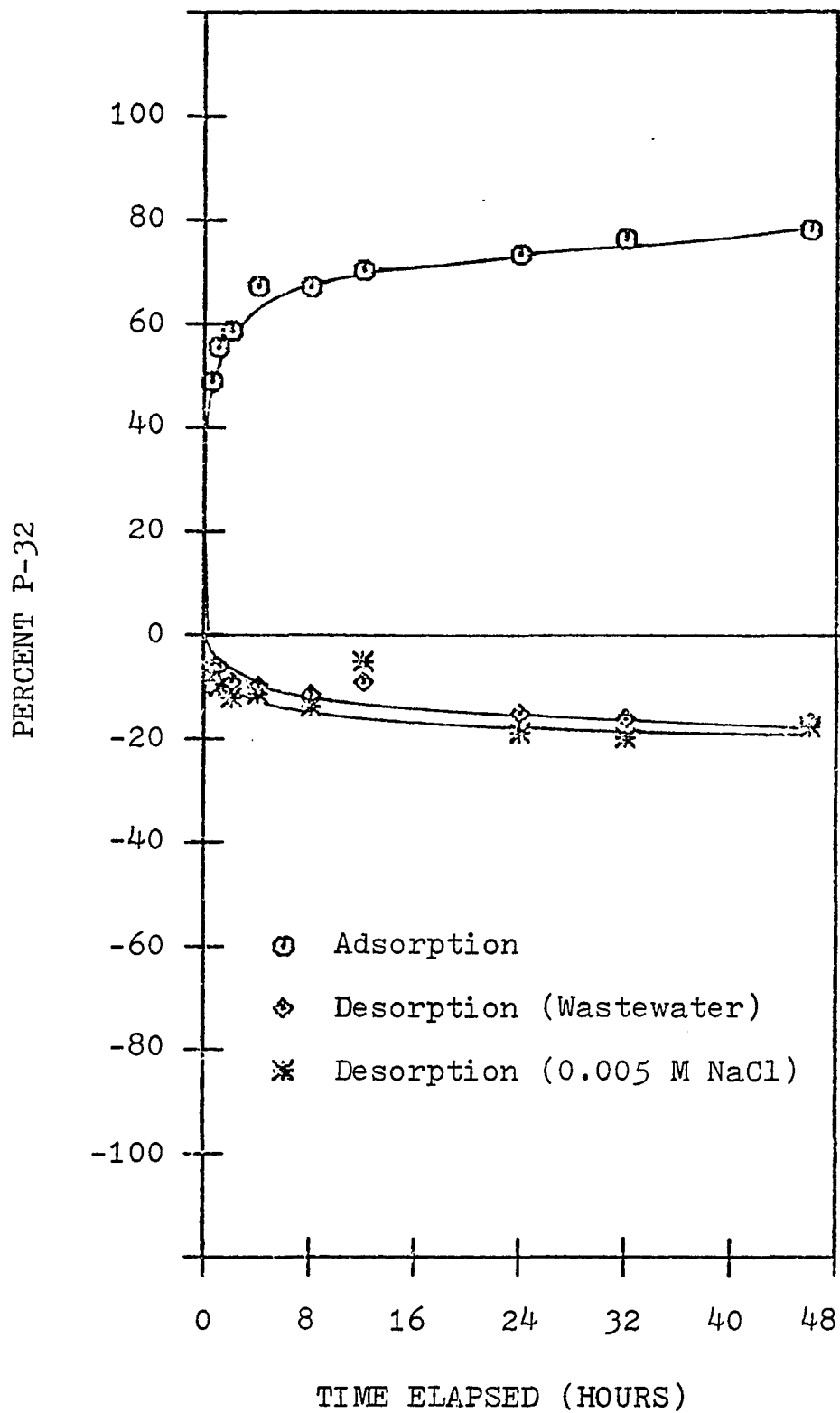


Figure 21. Adsorption - Desorption Behavior of P-32 with Tujunga Soil at pH 8.0.

solution in most of the isotherm studies. While no definitive explanation for this can be offered, it is interesting to speculate on the possibility that the speciation of phosphate, i.e. H_2PO_4^- vs HPO_4^{2-} , has an effect on the isotope exchange process where P is loosely bound.

CHAPTER VI

DETERMINATION OF REDUCED IRON BY MOSSBAUER SPECTROSCOPY

Introduction

One of the initial goals of this research project was to evaluate the effects of reducing conditions in soil systems and the resulting reduction of iron (III) to iron (II) on the sorption of phosphate from solution. As discussed in Chapter 2, several workers have related the reduction of iron in soils to decreased retention of phosphate. Since some wastewater application systems flood the fields used for treatment, reducing conditions can develop under waterlogged conditions (Whisler, et al., 1974). A study of phosphate sorption by Charlton and Tujung soils under reducing conditions would be of interest in explaining their overall sorption behavior.

Mossbauer spectroscopy allows the measurement of the relative abundance of iron in different chemical environments. It is an attractive method for the study of soils

due to the minimal amount of sample preparation required. Mossbauer spectroscopy has been successfully applied to the measurement of the relative amounts of iron (III) to iron (II) in soils and sediments (Burns, 1972; Kodama, et al., 1977; Manning, 1977).

Determining the total amount of iron present in soil is a relatively simple procedure. The relative abundances of Fe (II) to Fe (III) determined by Mossbauer can then be used in combination with the total amount of iron to determine the absolute amounts of the forms of iron present. Conventional determinations of Fe (II) versus Fe (III) concentrations in soils are dependent on extraction methods. As in many soil analysis methods, these extractions yield operational definitions of the iron extracted and have questionable specificity. Thus, accurate determinations of the amounts of reduced iron present in soils are difficult (Gotoh and Patrick, 1974). The Mossbauer procedure is potentially a better method than these extraction methods to monitor accurately the amounts of reduced iron present.

Experimental Procedures

Soil samples for Mossbauer spectroscopic determinations were prepared by filtering a soil suspension through a nitrocellulose filter to produce a suitably thin (~1 mm) and uniform layer of soil on the filter. The filters and deposited soil were placed in "PetrislidesTM" obtained

from the Millipore Corporation, Bedford, MA. This container, which holds the filter firmly in a flat position, was then placed in a vacuum dessicator for 12 hours to dry the sample (necessary for good spectra). The container was then sealed to prevent any further interaction with the atmosphere.

To evaluate the feasibility of using Mossbauer spectroscopy for estimating reducible iron in soils, a sample of Charlton soil deposited on a membrane filter was treated with several drops of 1 M hydroxylamine hydrochloride for several minutes to reduce a portion of the iron (III) present. The sample was then vacuum dried and sealed in a Petrislide as described above.

All Mossbauer spectra were produced using a Model AME - 40 Mossbauer spectrometer manufactured by Elscint, Ltd. Haifa, Israel.

Results and Discussion

Mossbauer spectra were successfully obtained for the soil samples. The spectra clearly show the characteristic doublets produced by Fe (III) and Fe (II) (Figures 22 and 23). Since much of the iron present in soil clays is associated with the hydrous iron oxide coatings of the particles, the observed spectra for untreated soils are representative of the reactive iron fraction of the soil responsible for sorption of phosphate.

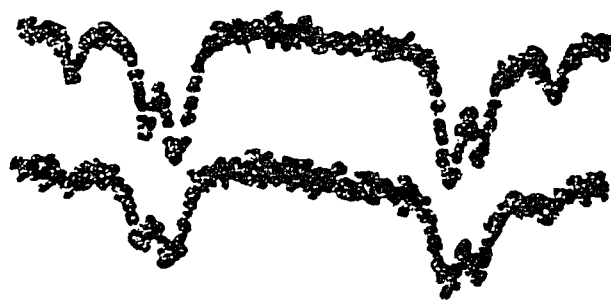


Figure 22. Mossbauer Spectra:
Top - Untreated Charlton Soil
Bottom - Untreated Tujunga Soil

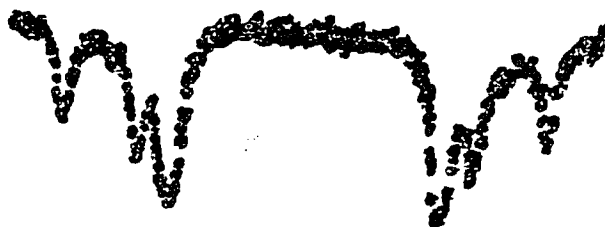


Figure 23. Mossbauer Spectrum:
Charlton Soil After Treatment
with Hydroxylamine Hydrochloride.
Outer Peaks Indicate Abundance of
Fe(II) in Sample.

An increased relative concentration of Fe (II) in the soil sample treated with hydroxylamine hydrochloride demonstrates that Mossbauer spectroscopy promises to be a method of determining iron oxidation states in soil. The outer peaks of the spectrum of the treated soil are significantly larger, indicating the increased relative abundance of reduced iron.

A major problem with routine application of Mossbauer Spectroscopy is the time required to obtain good spectra. Mossbauer is a time consuming technique, at best, requiring on the order of four hours to obtain a spectrum of an ideally suited, pure iron sample. This time requirement is inherent in the technique because only absorption due to iron-57 is actually observed. Since Fe-57 has a natural abundance of only about 2%, lengthy counting times are required to obtain satisfactory signal-to-background resolution for the gamma ray absorption. The examination of soils with their relatively low iron content and complex structure requires an apparent minimum of 48 hours, with longer times, up to as much as several weeks, desirable for a spectrum of good definition.

These studies were also limited because the available Cobalt-57 gamma ray source had an activity of only about 1 millicurie. Most Mossbauer spectroscopy studies employ sources with activities between 30 and 100 millicuries. Sources of higher activity reduce the time needed to obtain

adequate counting statistics.

Some manipulation of the soil samples could also reduce the requirements for obtaining good spectra. Examination of only the silt and clay fractions of the soil instead of the whole soil would help due to the larger proportion of iron present in these soil particles. The disadvantage of this approach is the separation step required to isolate the silt and clay. This somewhat defeats the advantage of minimal sample manipulation since the potential for atmospheric exposure is increased. Another possible way to shorten the time required for good spectra is to apply iron coatings to the soil particles enriched in Fe-57. This would substantially enhance the absorption per unit weight of sample but the modified particles might not accurately mimic the behavior of unaltered particles.

Other techniques of sample preparation are possible. For example, Manning (1977) employed freeze-dried sediment samples. However, our experience to date indicates that the procedure described above is quite satisfactory from a manipulative point of view and yields spectra of good quality given the limitations in the instrumentation used. The necessity of drying the samples can also limit the overall usefulness of the technique. Mossbauer spectra cannot be obtained for liquid or gelatinous samples. However, the hydrous iron oxides associated with clay particles contain large quantities of water in their

non-rigid structure. Thus the act of drying the samples substantially alters the internal structure of the soil fractions being examined.

In addition to the problems encountered with the use of the Mossbauer spectrometer, the study of phosphate sorption in soil systems under reducing conditions was deferred for a variety of procedural problems and equipment limitations. All such studies must be carried out under carefully controlled oxygen free conditions. This necessitates the use of elaborate atmosphere control systems such as designed and employed by Patrick and coworkers (Gotoh and Patrick, 1974; Patrick and Khalid, 1974). Alternative procedures might be carried out in more conventional controlled atmosphere glove boxes but they are not trivial extensions of open air techniques. Thus, due to the magnitude of the procedural developments and limitations of available equipment, the decision was made to discontinue this phase of the research.

CHAPTER VII

CONCLUSIONS

The particulate phase of sewage effluent appears relatively inactive in the phosphate binding process since no significant change in phosphate distribution occurs with changes in pH. Exchange of P-32 from the soluble to the particulate phase is also very low but increases (a) with total soluble P concentration, (b) with increases in pH, and (c) in the presence of bacterial action.

The Charlton soil is capable of rapidly binding effluent phosphate at pH from 5.0 to 8.0. However, binding is less complete at pH 8.0 than at lower pH. Desorption studies using reequilibration of soil with NaCl solution demonstrate that the sorbed P is very strongly bound. Isotope exchange studies show a steadily increasing amount of exchangeable phosphate present with increasing amounts of sorbed phosphate. Much of the behavior of the Charlton soil can be satisfactorily explained by the three mechanism sorption scheme of Ryden, et al. (1977a). With dormant periods such as those normally present in wastewater land treatment systems, it appears that the rate

of P sorption on Charlton soil would be more than adequate to maintain high quality renovation of wastewater for phosphate.

Tujungang soil sorbs smaller amounts of phosphate and at a slower rate than the Charlton soil. Decreasing pH decreases phosphate sorption at low phosphate levels typical for sewage effluents. This pH effect is the inverse of the behavior of the Charlton soil. At high amounts of sorbed phosphate, there is no apparent pH effect on the behavior of the Tujungang soil. Desorption studies show that the sorbed phosphate is weakly bound at all levels of addition and subject to a large amount of exchange and desorption. The behavior of the Tujungang soil can be partially explained by the physical sorption mechanism of Ryden, et al., coupled with assumptions about the solubility of phosphate compounds. However, a definitive explanation based on all the information obtained is not possible. In contrast to the Charlton soil, dormant periods cannot be expected to revitalize the Tujungang soil probably because the sorbed P is not transformed from physical sorbed forms to chemisorbed forms.

Interpretation of these results in terms of use of the soils for typical wastewater land treatment systems indicates that the Charlton soil is well suited for phosphate removal. However, use of the Tujungang soil would be expected to result in very unsatisfactory performance.

Continual application of wastewater may cause displacement of previously sorbed phosphate. Also, if the pH of the applied effluent falls below 6.0, large amounts of phosphate, including native P, may be mobilized. These conclusions account for the poor performance of the Manteca, California wastewater treatment site reported by Murrmann and Iskandar (1976).

Complementary use of radiotracers and spectrophotometric measurement for the study of sorption kinetics provided much information not obtainable by either method of analysis alone. The amount of exchange occurring concurrent with the sorption process was shown by the differences in the relative amounts of P-32 and spectrophotometrically determined phosphate removed from solution. The behavior of the P-32 reflected the movement of the phosphate which was initially in solution. Spectrophotometric determinations showed the net changes in solution concentration due to the combined effects of sorption by the soil and release from the soil.

During the desorption studies, behavior of the sorbed P-32 indicated the stability of the freshly sorbed phosphate as distinct from the stability of the native phosphate. The spectrophotometric measurements monitor the desorption of both the freshly sorbed and native phosphate.

Mossbauer spectroscopy appears to be a satisfactory technique for determining the concentration of reduced iron in a soil. Satisfactory spectra can be obtained with a minimal amount of sample handling. However, the instrumentation available for this project was marginally adequate.

All of these processes must be examined to gain a complete understanding of the phosphate sorbing abilities of soils. The stability of native phosphate is of great importance in evaluating a soil to be used in wastewater treatment.

LITERATURE CITED

- Anderson, M.R., 1978. A Case Study of Soil Phosphorus and Heavy Metals Due to Extended Effluent Irrigation, Land Treatment of Wastewater, International Symposium, Hanover, NH, V.2, 1-7.
- Asami, T., 1970. Behavior of Free Iron Oxide in Paddy Soil. Part II. Relations Between Reduced Free Iron Oxide and Changes in Eh, pH, and Ammonia in Paddy Soil, Soil Sci. and Plant Nutr., 16, 225 .
- Atkinson, R.J., Parfitt, R.L., and Smart, R.St. C., 1974. Infra-red Study of Phosphate Adsorption on Goethite. J. Chem. Soc. Faraday I, 70:1472-1479.
- Ballard, R., and Fiskell, J.G.A., 1974. Phosphorus Retention in Coastal Plain Forest Soils: I. Relationship to Soil Properties Soil Sci. Soc. Am. Proc., 38:250-255.
- Baillo, C.R., Waters, R.G., Iskandar, I.K., and Uiga, A., 1976. Preliminary Evaluation of 88 Years Rapid Infiltration of Raw Municipal Sewage at Calumet, Michigan, Eight Annual Cornell University Waste Management Conference, Rochester, New York.
- Ballaux, J.C. and Peaslee, D.E., 1975. Relationships Between Sorption and Desorption of Phosphorus in Soils, Soil Sci. Soc. Am. Proc., 39:275-278.
- Barrow, N.J., 1974. Effect of Previous Additions of Phosphate on Phosphate Adsorption by Soils, Soil Sci., 118:82-89.
- Barrow, N.J., 1979a. The Description of Desorption of Phosphate from Soil. J. Soil Sci. 30:259-270
- Barrow, N.J., 1979b. Three Effects of Temperature on the Reactions between Inorganic Phosphate and Soil. J. Soil Sci., 30:271-279.
- Barrow, N.J. and Shaw, T.C., 1975a. The Slow Reactions between Soil and Anions: 2. Effect of Time and Temperature on the Decrease in Phosphate Concentration in the Soil Solution. Soil Sci. 119:167-177.
- Barrow, N.J. and Shaw, T.C., 1975b. The Slow Reactions between Soil and Anions; Part III. The Effects of Time and Temperature on the Decrease in Isotopically Exchangeable Phosphate, Soil Sci. 119:190-197.

- Barrow, N.J., and Shaw, T.C., 1979b. Effects of Ionic Strength and Nature of the Cation on Desorption of Phosphate from Soil. *J. Soil Sci.* 30:53-65.
- Barrow, N.J., and Shaw, T.C., 1979c. Effects of Solution: Soil Ratio and Vigour of Shaking on the Rate of Phosphate Adsorption by Soil, *J. Soil Sci.*, 30:67-76.
- Bastian, R.K., 1978. An Overview of Monitoring Land Treatment Systems, *Land Treatment of Wastewater, International Symposium, Hanover, NH, V.1*, 347-354.
- Black, C.A., Ed., 1965. Methods of Soil Analysis. Agronomy Series No.9, American Society of Agronomy, Madison, Wi,
- Black, C.A., 1968. *Soil-Plant Relationships*, John Wiley Sons, Inc.
- Bolt, G.H., and Bruggenwert, M.G.M., Ed., 1976. *Soil Chemistry A. Basic Elements, Developments in Soil Science, V.5A*. Elsevier Scientific Publishing Co. New York.
- Bouwer, H., and Chaney, R.L., 1974. Land Treatment of Wastewater, *Advances in Agronomy*, 26:133-176.
- Brinkman, R., 1970. Ferrollysis; A Hydromorphic Soil Forming Process, *Geoderma*, 3:199-206.
- Burns, R.G., 1972. Mixed Valencies and Site Occupancies of Iron in Silicate Minerals from Mossbauer Spectroscopy, *Can. J. Spect.*, 17:51-59.
- Chang, S.C., and Jackson, M.L., 1957. Fractionation of Soil Phosphorus, *Soil Sci.*, 84:133-144.
- Daniels, F., and Alberty, R.A., 1966. Physical Chemistry, 3rd ed. John Wiley and Sons, Inc., New York, 286-291.
- Dryden, F.D., and Chen, C., 1978. Groundwater Recharge with Reclaimed Waters from the Pomona, San Jose Creek, and Whittier Narrows Plants, *Land Treatment of Wastewater International Symposium, August 1978 Hanover, NH, V.1*, 241 .
- Enfield, C.G., Harlin, C.C., Bledsoe, B.E., 1976. Comparison of Five Kinetic Models for Orthophosphate Reactions in Mineral Soils, *Soil Sci. Am. Proc.*, 40:243-249.
- Enfield, C.G., 1974. Rate of Phosphorus Sorption by Five Oklahoma Soils, *Soil Sci. Soc. Am. Proc.*, 38:404-407.

- Enfield, C.G., 1977. Wastewater Phosphorus Removal Using Land Application, Civil Eng. ASCE, June, 58-60.
- Enfield, C.G., 1978. Evaluation of Phosphorus Models for Prediction of Percolate Water Quality in Land Treatment, Land Treatment of Wastewater, International Symposium, Hanover, NH, V.1, 153-162.
- Enfield, C.G., and Shew, D.C., 1975. Comparison of Two Predictive Nonequilibrium One-Dimensional Models for Phosphorus Sorption and Movement through Homogeneous Soils, J. Environ. Qual., 4:198-202.
- Gakstatter, J.H., Allum, M.O., Dominguez, S.E., Crouse, M.R., 1978. A Survey of Phosphorus and Nitrogen Levels in Treated Municipal Wastewater, J. Water Pollution Control Fed. 50:718-720.
- Gaudette, H.E., Flight, W.R., Toner, L., and Folger, D.W., 1974. An Inexpensive Titration Method for the Determination of Organic Carbon in Recent Sediments, J. Sedimentary Petrology, 44:249-253.
- Goodman, B.A., and Cheshire, M.V., 1979. A Mossbauer Spectroscopic Study of the Effect of pH on the Reaction Between Iron and Humic Acid in Aqueous Media, J. Soil Sci., 30:85-91.
- Gotoh, S., 1973. Reduction Processes in Waterlogged Soils with Special Reference to Transformations of Nitrate, Manganese, and Iron, Bull. Kyushu Agr. Expt. Sta. 16:669-714.
- Gotoh, S., and Patrick, W.H., Jr., 1974. Transformation of Iron in a Waterlogged Soil as Influenced by Redox Potential and pH. J. Soil Sci., 38:66-70.
- Harter, R.D., and Baker, D.E., 1977. Applications and Misapplications of the Langmuir Equation to Soil Adsorption Phenomena, Soil Sci. Soc. Am. J., 41:1077-1080.
- Hsu, P.H., 1965. Fixation of Phosphate by Aluminum and Iron in Acidic Soils, Soil Sci., 99:398-402.
- Hsu, P.H., 1973. Complementary Role of Iron (III), Sulfate, and Calcium in Precipitation of Phosphate from Solution. Environ. Letters, 5:115-136.
- Hsu, P.H., and Rennie, D.A., 1962a. Reactions of Phosphate in Aluminum Systems: Part I. Adsorption of Phosphate by X-Ray Amorphous Aluminum Hydroxide, Can. J. Soil Sci., 42:197-209.

- Hsu, P.H., and Rennie, D.A., 1962b. Reactions of Phosphate in Aluminum Systems. II. Precipitation of Phosphate by Exchangeable Aluminum on a Cation Exchange Resin. *Can. J. Soil Sci.*, 42:210-221.
- Iskandar, I.K., 1978. Overview of Existing Land Treatment Systems, Land Treatment of Wastewater, International Symposium, Hanover, NH, V.1, 193-200.
- Iskandar, I.K., Sletten, R.S., Legget, D.C., Jenkins, T.F., 1976. Wastewater Renovation by a Prototype Slow Infiltration Land Treatment System, CRREL Report 76-19, Cold Regions Research and Engineering Laboratory, Hanover, NH .
- Iskandar, I.K., and Syers, J.K., 1980. Effectiveness of Land Treatment for Phosphorus Removal from Municipal Wastewater at Manteca, California, *J. Environ. Qual.* In Press.
- Kodama, H., McKeague, J.A., Tremblay, R.J., Gosselin, J.R., and Townsend, M.G., 1977. Characterization of Iron Oxide Compounds in Soils by Mossbauer and Other Methods, *Can. J. Earth Sci.*, 14:1-15.
- Kuo, S., and Lotse, E.G., 1972. Kinetics of Phosphate Adsorption by Calcium Carbonate and Ca-Kaolinite, *Soil Sci. Soc. Am. Proc.*, 36:725-729.
- Kuo, S., and Mikkelsen, D.S., 1979. Distribution of Iron and Phosphorus in Flooded and Unflooded Soil Profiles and Their Relation to Phosphorus Adsorption, *Soil Sci.*, 127, 18 .
- Larkin, E.P., Tierney, J.T., Lovett, J., Van Donsel, D., Fand Francis, D.W., 1978. Land Application of Sewage Wastes: Potential for Contamination of Foodstuffs and Agricultural Soils by Viruses, Bacterial Pathogens, and Parasites, Land Treatment of Wastewater, International Symposium, Hanover, NH, V.2, 215-223.
- Lindsey, W.L., and Moreno, E.C., 1960. Phosphate Phase Equilibrium in Soils, *Soil Sci. Soc. Am. Proc.*, 24:177-182.
- Lindsey, W.L., Frazier, A.W., and Stephenson, H.F., 1962. Identification of Reaction Products from Phosphate Fertilizers in Soils, *Soil Sci. Soc. Am. Proc.* 26:446-452.
- Longworth, G., Becker, L.W., Thompson, R., Oldfield, F., Dearing, J.A., and Rummery, T.A., 1979. Mossbauer Effect and Magnetic Studies of Secondary Iron Oxides in Soils, *J. Soil Sci.*, 30:93-110.

- Mackenzie, A.F., 1962. Inorganic Soil Phosphorus Fractions of Some Ontario Soils as Studied Using Isotopic Exchange and Solubility Criteria, *Can. J. Soil Sci.*, 42:150-156.
- Madrid, L, and Posner, A.M., 1979. Desorption of Phosphate from Goethite, *J. Soil Sci.*, 30:697-707.
- Mahapatra, I.C., and Patrick, W.H., Jr., 1969. Inorganic Phosphate Transformation in Waterlogged Soils, *Soil Sci.*, 107:281-288.
- Manning, P.G., 1977. Mossbauer Spectral Studies of Ferric-Phosphate Interaction in Sediments Underlying Oxidic Lake Waters, *Can. Mineral.*, 15:422-426.
- Mattingly, G.E.G., Labile Phosphate in Soils, *Soil Sci.*, 119:369-374.
- McLaughlin, J.R., Ryden, J.C., and Syers, J.K., 1977. Development and Evaluation of a Kinetic Model to Describe Phosphate Sorption by Hydrous Ferric Oxide Gel, *Geoderma*, 18:295-307.
- McLaughlin, J.R., and Syers, J.K., 1978. Stability of Ferric Phosphates, *J. Soil Sci.*, 29:499-504.
- Mehra, O.P., and Jackson, M.L., 1960. Clays Clay Min. 7:317-327.
- Murphy, J., and Riley, J.P., 1962. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters, *Anal. Chim. Acta*, 27, 30 .
- Murrmann, R.P., and Iskandar, I.K., 1976. Land Treatment of Wastewater. Case Studies of Existing Disposal Systems at Quincy WA, and Manteca, CA. Proceedings of the 1976 Cornell Agricultural Waste Management Conference, 467-488.
- Murrmann, R.P., and Peech, M., 1968. Reaction Products of Applied Phosphate in Limed Soils, *Soil Sci. Soc. Am. Proc.*, 32:493-496.
- Nissenbaum, A., 1979. Phosphorus in Marine and Non - Marine Humic Substances. *Geochim. et Cosmochim. Acta.* 43:1973-1978.
- Novak, L.T., Adriano, D.C., Coulman, G.A., and Shah, D.B., 1975. Phosphorus Movement in Soils: Theoretical Aspects, *J. Environ. Qual.*, 4:93-99.
- Novak, L.T., and Adriano, D.C., 1975b. Phosphorus Movement in Soils: Soil-Orthophosphate Reaction Kinetics, *J. Environ. Qual.*, 4:261-266.

- Nur, R., and Bates, M.H., 1979. The Effect of pH on the Aluminum, Iron, and Calcium Phosphate Fractions of Lake Sediments, *Water Research*, 13:813-815.
- Olsen, B.H., and Guinn, V.P., 1978. Accumulation of Trace Elements in Soil and Plants from Land Disposal of Secondary Domestic Wasterwater, *Land Treatment of Wastewater, International Symposium, Hanover, NH, V.2*, 289-299.
- Olsen, S.R., and Watanabe, F.S., 1957. A Method to Determine a Phosphorus Adsorption Maximum of Soils as Measured by the Langmuir Isotherm, *Soil Sci. Soc. Am. Proc.*, 21:144-149.
- Parfitt, R.L., Atkinson, R.J., and Smart, R.St.C., 1975. The Mechanism of Phosphate Fixation by Iron Oxides, *Soil Sci. Soc.Am.Proc.*, 39:837-841.
- Patrick, W.H., Jr., and Khalid, R.A., 1974. Phosphate Release and Sorption by Soils and Sediments: Effects of Aerobic and Anaerobic Conditions, *Science*, 186:53-55.
- Ponnamperuma, F.N., 1972. The Chemistry of Submerged Soils, *Advances in Agronomy*, N.C.Brady, Ed., 24:29-96.
- Rand, J.C., Greenberg, A.E., and Taras, M.J., Eds., 1975. Standard Methods for the Examination of Water and Wastewater, 14th ed. APHA-AWWA-WPCF .
- Reed, S., Murrmann, P., Koutz, F., Rickard, W., Hunt, P., Buzzell, T., Carey, K., Buda, S., Guter, K., and Sorber, C., 1972. *Wastewater Management by Disposal on Land. Special Report 171, Corps of Engineers, U.S. Army, Cold Regions Research and Engineering Laboratory, Hanover, NH.*
- Ryden, J.C., McLaughlin, J.R., and Syers, J.K., 1977a. Mechanisms of Phosphate Sorption by Soils and Hydrous Ferric Oxide Gel, *J. Soil Sci.*, 28:72-92.
- Ryden, J.C., McLaughlin, J.R., and Syers, J.K., 1977b. Time-Dependent Sorption of Phosphate by Soils and Hydrous Ferric Oxides, *J. Soil Sci.*, 28:585-595.
- Ryden, J.C., and Syers, J.K., 1975. Rationalization of Ionic Strength and Cation Effects on Phosphate Sorption by Soils, *J. Soil Sci.*, 26:395-406.
- Ryden, J.C., and Syers, J.K., 1977c. Origin of the Labile Phosphate Pool in Soils, *Soil Sci.*, 123:353-361.

- Ryden, J.C., and Syers, J.K., 1977d. Desorption and Isotopic Exchange Relationships of Phosphate Sorbed by Soils and Hydrous Ferric Oxide Gel, *J. Soil Sci.*, 28:596-609.
- Ryden, J.C., Syers, J.K., and McLaughlin, J.R., 1977e. Effects of Ionic Strength On Chemisorption and Potential-Determining Sorption of Phosphate by Soils, *J. Soil Sci.* 28:62-71.
- Sawyer, C.N., 1966. Basic Concepts of Eutrophication, *J. Water Pollution Control Fed.* 38:737-744.
- Schmidt, C.J., Kugelman, I., and Clements, E.V.III, 1975. Municipal Wastewater Reuse in the U.S., *J. Water Pollution Control Fed.*, 47:2229-2245.
- Shah, D.B., Coulman, G.A., Novak, L.T., and Ellis, B.G., 1975. A Mathematical Model for Phosphorus Movement in Soils, *J. Environ. Qual.*, 4:87-92.
- Sopper, W.E., and Kardos, L.T., 1973. Recycling Treated Municipal Wastewater and Sludge through Forest and Cropland, Pennsylvania University Press.
- Sopper, W.E., and Richenderfer, J.L., 1979. Effect of Municipal Wastewater Irrigation on the Physical Properties of the Soil, Utilization of Municipal Sewage Effluent and Sludge on Forest and Disturbed Land, The Penn.State U.Press, University Park and London 179-195.
- Syers, J.K., Harris, R.F., and Armstrong, D.E., Phosphate Chemistry in Lake Sediments, *J. Environ. Qual.*, 2, 1 .
- Tofflemire, T.J., and Farnan, R.A., 1975. Land Disposal of Wastewater, *J. Water Pollution Control Fed.*, 47:1344-1368.
- Turner, F.T., and Patrick, W.H., Jr., 1968. Chemical Changes in Waterlogged Soils as a Result of Oxygen Depletion, *Trans. 9th Intern. Congress of Soil Sci.*, Vol IV, 53, 4.
- Urie, D.H., Cooley, J.H., and Harris, A.R., 1978. Irrigation of Forest Plantations with Sewage Lagoon Effluents, *Land Treatment of Wastewater, International Symposium, Hanover, NH, V.2*, 207-213.
- Van Riemsdijk, W.H., Weststrate, F.A., and Beek, J., 1977. Phosphate in Soils Treated with Sewage Water: III. Kinetic Studies on the Reaction of Phosphate with Aluminum Compounds, *J. Environ. Qual.* 6:26-29.

- Vijayachandran, P.K., and Harter, R.D., 1975. Evaluation of Phosphorus Adsorption by a Cross Section of Soil Types, *Soil Sci.*, 119:119-125.
- Weir, C.C., and Black, C.A., 1968. Mineralization of Organic Phosphate in Soils as Affected by Addition of Inorganic Phosphorus, *Soil Sci. Soc. Am. Proc.* 32:51-55.
- Weir, C.C., and Soper, R.J., 1962. Adsorption and Exchange Studies of Phosphorus in Some Manitoba Soils, *Can. J. Soil Sci.*, 42:31-42.
- Whisler, F.D., Lance, J.C., and Linebarger, R.S., 1974. Redox Potentials in Soil Columns Intermittently Flooded with Sewage Water. *J. Environ. Qual.*, 3:68-74.
- White, R.E., and Taylor, A.W., 1977a. Effect of pH on Phosphate Adsorption and Isotopic Exchange in Acid Soils at Low and High Additions of Soluble Phosphate, *J. Soil Sci.*, 28:48-61.
- White, R.E., and Taylor, A.W., 1977b. Reactions of Soluble Phosphate with Acid Soils: The Interpretation of Adsorption-Desorption Isotherms, *J. Soil Sci.*, 28:314-328.
- Williams, J.D.H., Syers, J.K., and Walker, T.W., 1967. Fractionation of Soil Inorganic Phosphate by a Modification of Chang and Jackson's Procedure, *Soil Sci. Soc. Am. Proc.*, 31:736-739.

APPENDIX A

Charlton Soil Adsorption Isotherms; 24 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
<0.04	24.0	<0.04	24.0	0.13	22.7
0.80	266.	1.28	261.	0.14	22.6
0.63	268.	1.16	262.	3.45	239.
1.22	512.	3.16	492.	12.2	402.
1.28	511.	3.06	493.	11.8	406.
4.73	477.	13.2	542.	9.98	424.
4.26	481.	24.5	629.	20.5	469.
8.81	586.	24.7	627.	18.1	493.
17.8	696.	23.0	794.	32.4	550.
14.0	884.	35.8	666.	35.8	666.
13.6	888.				

Charlton Soil Adsorption Isotherms; 48 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
<u>Solution Conc. (mg P/L)</u>	<u>P Sorbed (ug P/g Soil)</u>	<u>Solution Conc. (mg P/L)</u>	<u>P Sorbed (ug P/g Soil)</u>	<u>Solution Conc. (mg P/L)</u>	<u>P Sorbed (ug P/g Soil)</u>
<0.04	24.0	<0.04	24.0	0.25	21.5
0.38	271.	0.82	266.	0.23	217.
0.54	269.	0.86	265.	3.02	244.
0.87	515.	3.15	493.	15.8	516.
0.80	516.	2.22	502.	15.8	516.
2.92	495.	8.86	585.	9.90	425.
2.10	503.	18.1	693.	8.70	437.
4.99	624.	19.6	678.	7.78	446.
5.86	615.	26.4	760.	26.8	606.
13.3	741.	20.8	816.	32.5	699.
10.9	915.	18.8	836.	36.9	655.
10.6	918.				

Charlton Soil Adsorption Isotherms; 72 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
<0.04	24.0	<0.04	24.0	0.20	22.0
0.30	272.	0.70	267.	0.21	21.9
0.37	270.	0.72	267.	3.13	243.
0.63	518.	7.80	596.	9.28	431.
0.57	518.	15.2	722.	8.40	440.
2.09	503.	17.3	701.	8.22	442.
1.33	511.	22.9	795.	15.3	521.
4.14	633.	18.8	836.	25.2	622.
3.47	640.	16.1	863.	15.8	546.
9.80	776.			33.8	686.
7.97	944.			35.2	672.
8.31	941.				

Charlton Soil Adsorption Isotherms; 96 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
<0.04	24.0	<0.04	24.0	0.29	21.2
0.28	272.	0.68	267.	0.36	20.4
0.31	271.	0.68	267.	3.41	240.
0.55	519.	1.73	506.	8.44	440.
0.46	519.	1.60	508.	9.32	431.
2.41	650.	5.76	616.	8.66	437.
1.59	508.	14.3	731.	15.7	517.
1.02	514.	14.9	725.	15.6	518.
2.44	650.	17.2	852.	33.7	687.
7.98	794.	14.9	875.		
6.95	955.				

APPENDIX B

Tujungga Soil Adsorption Isotherms; 24 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
1.92	4.80	1.28	11.2	1.37	10.3
1.96	4.40	1.35	10.5	1.37	10.3
13.3	41.0	12.1	53.0	11.0	64.0
29.8	76.0	12.1	53.0	26.8	106.
46.5	59.0	28.2	92.0	28.8	86.0
46.1	63.0	44.9	75.0	39.6	128.
60.6	168.	44.4	80.0	38.0	144.
60.2	172.	62.4	150.	57.1	203.
91.2	112.	91.9	105.	85.9	165.
92.5	99.0	93.0	94.0	92.2	102.
		78.4	240.		
		88.2	142.		

Tujungsa Soil Adsorption Isotherms; 48 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
1.62	7.80	1.01	13.9	1.36	10.4
1.59	8.10	1.10	13.0	1.26	11.4
12.1	53.0	10.9	65.0	10.8	66.0
29.1	83.0	12.1	53.0	24.7	127.
45.9	65.0	25.6	118.	29.0	84.0
33.6	188.	41.6	108.	38.1	143.
62.8	146.	42.7	97.0	39.6	128.
66.7	107.	60.1	174.	58.9	185.
92.4	100.	91.7	107.	84.6	178.
92.3	101.	90.3	121.		
		89.9	125.		
		87.5	149.		

Tujungang Soil Adsorption Isotherms; 72 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
1.32	10.8	1.80	6.0	1.60	8.0
1.38	10.2	11.4	60.0	1.37	10.3
11.6	58.0	11.7	57.0	10.8	66.0
29.1	83.0	25.6	118.	24.3	131.
44.6	78.0	40.1	123.	29.4	80.0
40.3	121.	38.3	141.	41.7	107.
64.1	133.	60.1	173.	39.6	128.
57.0	204.	89.8	126.	59.0	184.
89.5	129.	93.9	85.0	83.4	190.
90.3	121.	89.0	134.	86.4	160.
		85.8	166.		

Tujungna Soil Adsorption Isotherms; 96 Hour Equilibration.

pH 5.0		pH 6.5		pH 8.0	
Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)	Solution Conc. (mg P/L)	P Sorbed (ug P/g Soil)
1.15	12.5	1.77	6.3	1.57	8.3
1.21	11.9	1.12	12.8	1.40	10.0
10.9	69.0	10.5	69.0	10.6	68.0
25.7	117.	11.5	59.0	22.7	147.
45.0	74.0	24.8	126.	26.4	110.
42.0	104.	41.8	106.	39.4	130.
58.5	189.	41.9	105.	35.7	167.
58.5	189.	58.9	185.	60.1	173.
87.9	145.	91.2	112.	85.1	173.
91.2	112.	81.5	209.		
		88.3	141.		

APPENDIX C

Charlton Soil: Exchangeable P Versus Sorbed P.

pH 5.0		pH 6.5		pH 8.0	
P Sorbed (ug P/g Soil)	P Exchange. (ug P/g Soil)	P Sorbed (ug P/g Soil)	P Exchange. (ug P/g Soil)	P Sorbed (ug P/g Soil)	P Exchange. (ug P/g Soil)
272.	100.	267.	129.	240.	149.
271.	65.	267.	152.	440.	248.
519.	132.	507.	149.	431.	215.
519.	120.	508.	195.	437.	228.
650.	259.	616.	235.	517.	230.
508.	193.	731.*	117.*	518.	223.
514.	147.	725.	282.	687.	309.
650.	204.	852.	388.		
794.	329.	875.	370.		
951.	445.				
955.	349.				

* Data point omitted in statistical calculations.

Tujungga Soil: Exchangeable P Versus Sorbed P.

pH 5.0		pH 6.5		pH 8.0	
P Sorbed (ug P/g Soil)	P Exchange. (ug P/g Soil)	P Sorbed (ug P/g Soil)	P Exchange. (ug P/g Soil)	P Sorbed (ug P/g Soil)	P Exchange. (ug P/g Soil)
12.5	19.5	6.3	35.3	8.3	18.1
11.9	18.3	12.8	17.7	10.0	16.4
65.0	34.4	69.0	46.3	68.0	45.2
117.	57.2	59.0	36.9	147.	41.
74.0	108.	126.	46.2	110.	38.1
104.	48.2	106.	48.0	130.	76.6
189.	33.4	185.	84.9	173.	114.
145.	70.2	112.	42.0		
112.	43.0	209.	27.8		
		141.	91.6		

Statistical Calculations: Evaluation of pH Effects on
P Exchangeability.

Least Squares Fit for Intercept = 0

$$\text{Slope } b_1 = \frac{\sum xy}{\sum x^2}$$

$$\text{Variance } S_{y_0}^2 = \frac{\sum y^2 - \frac{(\sum xy)^2}{\sum x^2}}{n-1}$$

Results for Charlton Soil

pH 5.0

$$b_1 = 0.3706$$

$$S_{y_0}^2 = 48.51 \text{ } \mu\text{g/g}$$

pH 6.5

$$b_1 = 0.3363$$

$$S_{y_0}^2 = 119.9 \text{ } \mu\text{g/g}$$

pH 8.0

$$b_1 = 0.4776$$

$$S_{y_0}^2 = 25.37 \text{ } \mu\text{g/g}$$

Pooled Values: pH 5.0 & 6.5

$$b_1 = 0.355$$

$$S_{y_0}^2 = 83.88$$

$$\text{Pooled Variance } S_{y_p}^2 = \frac{(S_{y_a}^2)(n_a - 1) + (S_{y_b}^2)(n_b - 1)}{(n_a - 1) + (n_b - 1)}$$

$$S_{y_p}^2 = 71.91$$

Test of Significance of Difference in Slopes (t Test)

$$t = \frac{b_1 - b_2}{(S_{y_p}^2) \left(\frac{1}{x_1^2} + \frac{1}{x_2^2} \right)^{\frac{1}{2}}} = 2.00$$

Tabular Value t (d.f.=24) (.90) = 1.71